# SIMULATION AND MULTIPLICITY OF STEADY STATES OF CSTRs FOR FREE RADICAL POLYMERIZATION WITH THE GEL EFFECT

A Thesis Submitted
in Partial Fulfilment of the Requirements
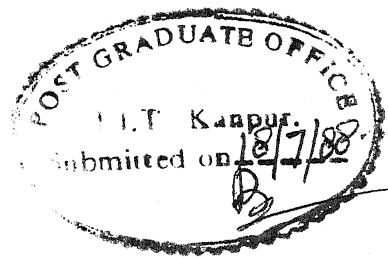for the Degree of

## MASTER OF TECHNOLOGY

*by*

SADHAN CHANDRA JANA

*to the*

**DEPARTMENT OF CHEMICAL ENGINEERING**
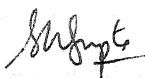
**INDIAN INSTITUTE OF TECHNOLOGY KANPUR**

**JULY, 1988**

## CERTIFICATE

This is to certify that the present work 'SIMULATION AND MULTIPLICITY OF STEADY STATES OF CSTRs FOR FREE RADICAL POLYMERIZATION WITH THE GEL EFFECT' has been carried out by Mr. Sadhan Chandra Jana under my supervision and this has not been submitted elsewhere for a degree.

July, 1988

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## ACKNOWLEDGEMENTS

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# CHAPTER V

## SUGGESTIONS FOR FURTHER STUDY

For the correct prediction of parameter values, for which the CSTRs exhibit five different patterns of study state multiplicity, a specific $\alpha$-$\beta$ plot is necessary. It can be generated by accounting for the stiffness of the functions $F$, $F_{x_i}$, $F_{xx_i}$ and $F_{Da}$ and simultaneous solution of the defining equations of hysteresis and isola varieties. Further, the study of stability of these multiple solutions is necessary for the efficient control of the reactor.

## NOMENCLATURE

| | |
|---|---|
| A, B | Dimensionless terms in the expression of C (Table II) |
| $c_p$ | Specific heat of the reaction mixture |
| Da | Damkohler number |
| $D_n$ | Dead polymer molecule having n repeating units |
| $E_d$ | Activation energy for initiator decomposition |
| $E_p$ | Activation energy of chain propagation |
| $E_t$ | Activation energy of chain termination |
| $E_{\theta_t}$, $E_{\theta_p}$ | Activation energies in $\theta_t$, $\theta_p$ expressions (Table II) |
| f | Initiator efficiency |
| $f_s$ | Solvent volume fraction in the feed |
| h | Heat transfer coefficient to reactor |
| $(-\Delta H_r)$ | Heat of propagation reaction |
| I | Initiator |
| $k_d$ | Initiator decomposition rate constant |
| $k_d^o$ | Pre-exponential factor of initiator decomposition rate constant |

$k_p$        Propagation rate constant

$k_{p_o}$        Propagation rate constant in absence of gel-effect

$k_{p_o}^o$        Pre-exponential factor of $k_{p_o}$

$k_t$        Termination rate constant

$k_{t_c}$        Combinational termination rate constant

$k_{t_d}$        Termination rate constant by disproportionation

$k_{t_o}$        Termination rate constant in absence of gel-effect

$k_{t_o}^o$        Pre-exponential factor of $k_{t_o}$

$M$        Monomer concentration

$P_n.$        Growing radical having n repeating units

$Q$        lit solution/min of product

$Q_m$        lit monomer/min in product

$Q_o$        lit solution/min of feed

$Q_p$        lit polymer/min in product

$Q_s$        lit solvent/min in product

$Q_{m_o}$        lit monomer/min in feed

$Q_{p_o}$        lit polymer/min in feed

$Q_{s_o}$        lit solvent/min in feed

$R.$        Primary radical

| | |
|---|---|
| R | Universal gas constant |
| S | Dimensionless parameter (Table IV) |
| T | Reactor temperature |
| $T_c$ | Coolant temperature |
| $T_f$ | Feed temperature |
| $T_m$, $T_p$ | Glass transition temperature of monomer and polymer respectively |
| V | Volume of the reactor |
| $V_f$ | Free volume fraction |
| $X_1$ | Conversion of monomer to polymer |
| $X_2$ | Fractional conversion of initiator |
| $X_3$ | Dimensionless temperature |

## Greek Letters

| | |
|---|---|
| $\alpha$ | Dimensionless heat transfer parameter |
| $\beta$ | Dimensionless heat of reaction |
| $\delta$ | Dimensionless coolant temperature |
| $\varepsilon$ | Dimensionless density change of the reaction mixture, $(\dfrac{\rho_p - \rho_m}{\rho_p})$. |
| $\Xi$ | $f_s/(1-f_s)$ |

$\emptyset_m$ — Volume fraction of monomer ($\dfrac{1-X_1}{1-\varepsilon X_1 + \xi}$)

$\emptyset_p$ — Volume fraction of polymer ($\dfrac{X_1(1-\varepsilon)}{1-\varepsilon X_1 + \xi}$)

$\rho_m$ — Density of the monomer at the reactor temperature

$\rho_{mo}$ — Density of the monomer at the feed temperature

$\rho_s$ — Density of solvent

$\Theta_p, \Theta_t$ — Characteristic migration times for propagation and termination respectively

$\Theta_p^o, \Theta_t^o$ — Pre-exponential factors of $\Theta_p$, $\Theta_t$ respectively

$\tau$ — Dimensionless mean residence time

$\lambda_o$ — Total concentration of the live polymer

$\xi$ — $f_s / (1 - f_s)$

Symbols

$\lceil \ \rceil$ — Concentration, mol/lit

$[ \ ]_o$ — feed concentration, mol/lit

Subscripts

m — Monomer

o — Inlet value

Supercripts

o — Pre-exponential value

# ABSTRACT

An attempt has been made to improve the gel and glass effect correlations of Chiu et al. Soong and coworkers adopted the model of Chiu et al. and used different values of the parameters in the correlations for $\theta_t$ and $\theta_p$. No consistent set of parameters were obtained in their studies. Improved parameter values obatined herein match the CSTR simulation results of Carrat et al. very well. Steady state multiplicity patterns of continuous flow stirred tank reactors (CSTRs) with gel effect are explored. Above an average conversion of 40%, the presence of gel effect cannot be neglected. Only hysteresis type multiplicity could be obtained using simulation results. The stiffness and sensitivity of the defining equations of hysteresis and isola varieties made it impossible to solve them numerically to give a bifurcation diagram.

# CHAPTER I

## INTRODUCTION

There has been a spate of research activity in the area of modeling and control of free radical polymerization reactors over the past few years. With the improved understanding of polymerization kinetics and reactor behaviour, aided by the implementation of sophisticated reactor control algorithms, current research is directed towards the control of polymer properties. For over four decades, both free radical bulk and solution polymerizations have been a matter of study. From the vast array of experimental data with different systems (e.g., polystyrene, PS, polymethyl methacrylate, PMMA) in this field, it is well established that the classical low conversion free radical kinetics[1,2] (See Table I for mechanism) cannot be applied over the entire course of the reaction, especially at high conversions. Even under isothermal conditions, many such polymerization systems exhibit a large autoacceleration of the rate of polymerization, associated with an increase in the molecular weight of the polymer produced. This autoacceleration, the result of a very rapid decrease in the rate constant associated with chain-termination ($k_{tc}$ and $k_{td}$) due to the introduction of severe diffusional limitations, is known as the gel or Trommsdorff[3] effect. With the progress of reaction beyond the gel-effect,

## TABLE I

## KINETICS OF FREE RADICAL POLYMERIZATION

INITIATION

$$I \xrightarrow{k_d} 2R\cdot$$

$$R\cdot + M \xrightarrow{k_i} P\cdot_1$$

PROPAGATION

$$P_j\cdot + M \xrightarrow{k_p} P_{j+1}\cdot$$

TERMINATION

$$P_i\cdot + P_j\cdot \xrightarrow{k_{td}} D_{i+j} \quad \text{by disproportionation}$$
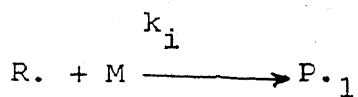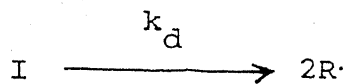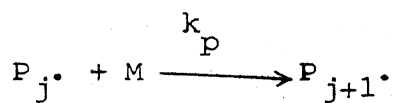
$$P_i\cdot + P_j\cdot \xrightarrow{k_{tc}} D_{i+j} \quad \text{by combination}$$
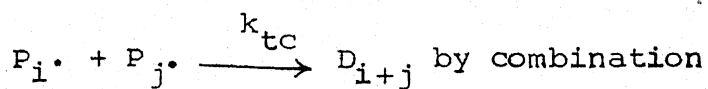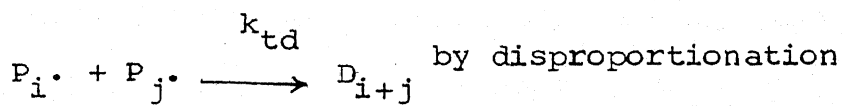
a point may be reached where even the diffusion of the monomer to the reactive radical sites is severely curtailed. This phenomenon accounts for a drastic decrease in the propagation rate constant, $k_p$, and is known as the glass effect. In the past few decades, several researchers have tried to explain experimental data by improving the kinetic model to account for the gel and glass-effects. All such improvements are backed by some physical assumptions. Friis and Hamielec[4] and Ross and Laurence[5] used simple empirical methods to describe such polymerization kinetics. They correlated an apparent termination rate constant with various system parameters, such as conversion, temperature and free volume. A second string of workers approached the problem of gel effect by making some empirical statements about the molecular weight and conversion dependence of the termination rate constant, $k_t$, using either qualitative analogies or experimental results on polymer transport phenomena or both. Of these workers, the work of Cardenas and O'Driscoll[6] (COD) and Marten and Hamielec[7] (MH) are important. In the COD model, the polymer species are divided into two populations, one with the degree of polymerization (DP) less than a critical value and the other with a degree of polymerization greater than the critical value. The critical degree of polymerization dictates the onset of the gel effect. The population with a DP less than $(DP)_{crit}$ is assigned a termination rate constant '$k_{t_o}$' which is the value in the

absence of the gel-effect. But the termination rate constant for the population with DP > $DP_{crit}$, $k_t$, the apparent rate constant, is an inverse function of the number-average degree of polymerization and the polymer volume fraction. In the MH model it is assumed that $k_t$ depends on the polymer concentration and molecular weight. Both these model are good in fitting experimental data, but are bsed on totally different and nonequivalent physical assumptions and use different dependences of $k_t$ upon concentration and molecular weight. However, the above models are empirical and are not tested against other solution properties of the system over the range of conditionsof the experiment. Moreover, in these models, the diffusion behaviour of the radicals has been expressed in an adhoc manner which is flexible enough so that it could be adjusted to fit experimental data. Tulig and Tirrel[8] developed a model using classical diffusion-controlled reaction kinetics and related the termination rate constant to the diffusion constant of the growing radical. The model can fit experimental data on conversion vs. time and molecular weight vs. conversion upto about 70 or 75% conversion. Besides these, a number of researchers[9-12] in an attempt to determine the effects of concentration, viscosity and molecular weight on the rate of polymerization, have carried out kinetic experiments. But even with such extensive research, a consistent understanding of the

molecular processes controlling the rate of polymerization could not emerge. Chiu et al.[13] recently focussed on this aspect and modeled this phenomena using a molecular view point. They developed a mathematical model to describe the gel and glass effects from a fundamental molecular phenomena. It does not need any artificially imposed break points either in the viscosity or in the molecular weight vs. concentration plots, to indicate the onset of diffusional limitations to the termination and propagation steps. Model parameters are linked to the operating variables of the process, especially to the reaction temperature. Moreover, one unified equation is sufficient to evaluate $k_p$ and $k_t$ for the entire course of the reaction. They have fitted the experimental data at all the three temperatures, 50°, 70° and 90°C, for which good isothermal batch data is available, using gross values of the model parameters. For these reasons , the model of Chiu et al.[13] is followed in the present work.

In the last two decades, remarkable progress has also been made in the understanding of the complex steady-state multiplicity patterns shown by continuous flow stirred tank reactors (CSTRs). For a single, exothermic, first order reaction occuring in a CSTR, changes in the flow rate (hence, residence time) can lead to complex multiplicity of steady-states of the reactor. Zeldovich and Zysin[14] were the first to indicate four different multiplicity patterns for a very

high activation energy of the reaction. Although earlier
unnoticed, this work was later confirmed by Furusawa and
Nishimura[15], and Hlavacek et al.[16]. Uppal, Ray and Poore[17]
developed an intricate scheme to investigate the multiplicity
pattern for any specific set of parameters, which was later
simplified by Huang and Varma[18]. Golubitsky and Keyfitz[19]
applied singularity theory to prove that, for such systems,
upto six different steady-state multiplicity patterns are
possible (Figure 1). However, their analysis cannot predict
the multiplicity pattern for any set of physical parameters
values. Balakotaiah and Luss[20] developed a simple technique
for the exact prediction of the multiplicity pattern for any
set a parameter values. They extended their technique to
find the multiplicity pattern for reactions with any rate
expression[21-25]. Although these are devoted only to single,
exothermic reactions, considerable progress has been made
in its application to polymerization reactors also. Indeed,
in recent years, steady state characteristics and dynamic
behaviour of various types of polymerization reactors have
been studied extensively[26-34]. Hamer et al.[30] studied the
free radical solution polymerization in CSTRs and identified
multiple steady states, limit cycles and oscillatory pheno-
mena depending upon the values of the solvent volume fraction
and the heat transfer parameter. They showed that upto six
different types of multiplicity patterns are possible.

X

Da
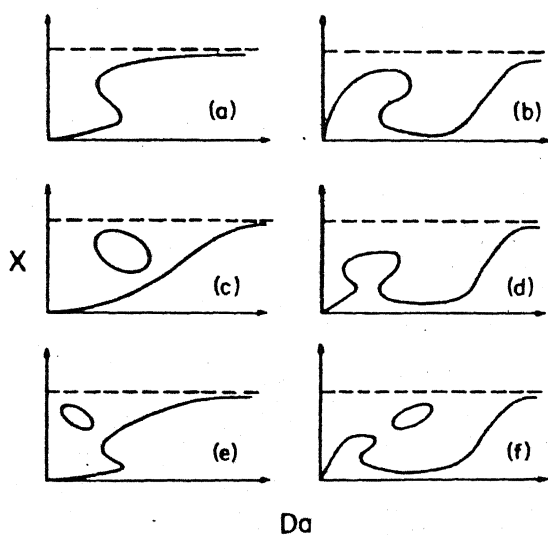
FIGURE 1 Schematic diagrams of the six possible multiplicity patterns.

Schmidt et al.[34] confirmed the isolated branch in the conversion vs. residence time plot (called isola) experimentally. They indicated that operating the reactor at isolas may help obtain high conversions at low residence times. They used coolant temperature, reactor heat transfer coefficient and feed solvent concentration as parameters and showed that these parameters can have an enormous effect on reactor behaviour. Jaisinghani and Ray[28] performed an analysis of the reactor behaviour by assuming that the initiator concentration remain unchanged for the course of the reaction i.e., initiator consumption is negligibly small. They argued that, in commercial practice, the effective initiator concentration in the reactor can be maintained nearly constant over a wide range of conversions, when the initiators are slowly decomposing and are used in high concentration in the feed. They identified the multiple steady states and unstable limit cycles. Recently, Choi[35] followed the technique of Balakotaiah and Luss[20] to investigate the multiplicity patterns of CSTRs for free radical solution polymerization. He developed the model for solution polymerization (solvent volume fraction $f_s > 0.6$) of methylmethacrylate with constant initiator concentration and no gel effect and analysed it using heat of reaction, heat transfer coefficient, coolant temperature and activation energies in the form of various dimensionless parameters. He identified five regions of parameter values which were

used to exhibit five different types of multiplicities. He
then applied the same methodology to the case of variable
initiator concentration i.e., when the change in the
initiator concentration cannot be neglected. However,
Choi's methodology does not have any provision to include
the gel effect. In fact, for bulk polymerization systems
or for solution polymerization systems with fs $<$ 0.6 , the
presence of gel effect cannot be overruled.

In the first part of the present work, an attempt
has been made to improve the correlations for the gel effect.
There are two parameters , $\theta_t$ and $\theta_p$ (See Table II) the
model of Chiu et al.[13] which need to be improved in order to
match experimental data on batch reactor In the second part, a study of
free radical solution polymerization of methyl methacrylate
in CSTRs has been carried out, with an objective of investi-
gating the steady state multiplicity patterns of the reactor.
The influence of both the gel and glass effects has been
accounted for in the present work, using Chiu et al's gel[13]
effect model with improved $\theta_t$ and $\theta_p$ correlations obtained
in the first part.

# CHAPTER II

## FORMULATION

The first step in formulation is to identify the
kinetic mechanism. The kinetics of free radical polymerization
is summarized in Table I. The reaction mechanism adopted
here consists of three major steps, characteristic of all
free radical polymerization processes. They are initiation,
propagation and termination. In the chain initiation step,
free radicals are generated by the thermal decomposition of
an initiator such as AIBN (2, 2' - azo bisis obutyronitrile).
They result in two primary free radicals, $R°$. In chain
propagation, primary radicals thus generated quickly react
with monomer to form long polymer radicals, $P_n$: Propagation
ends when either a glass is formed (and $k_p \rightarrow 0$) or an
equilibrium monomer concentration is reached. Termination
occurs when two radicals react via a bimolecular process.
Radicals could terminate via two paths. The microradicals
can combine to form a single dead polymer chain (called
combination) or form two dead chains (called disproportionation).
Although radical transfer to solvent and to monomer has to be
accounted for for accurate prediction of molecular weights,
in this study, for the sake of simplicity, these are neglected.
Also neglected are the branching reactions, thermal initiation
of monomer, and all other transfer reactions. These are not
expected to influence multiplicity characteristics significantly.

The second step is to develop the species mass balance and energy balance equations from the kinetic scheme of Table I. A CSTR of volume V is considered here with inlet and outlet streams as in Figure 2. The symbols are explained in the Nomenclature. Details of the balance equations are presented in Table II. A little reflection on the definitions of the Q and M terms shows that the volumetric flow rate of the product stream is given by the sum of the contributions of the monomer (m), polymer (p) and solvent (S):

$$Q = Q_m + Q_P + Q_S \qquad (1)$$

where

$$Q_S = \varepsilon \, Q_{mo} \qquad (a)$$

$$Q_P = \frac{M_o \, X_1}{\rho_P} \qquad (b)$$

$$Q_m = \frac{M_o \, (1 - X_1)}{\rho_m} \qquad (c) \qquad (2)$$

In Eqn. 2 $M_o \, X_1$ is the gm of monomer/min, being converted into polymer, $\varepsilon = f_s/(1-f_s)$, and $f_s$ is the volume fraction of solvent in the feed. It is assumed that the density of the solvent is constant, and that the feed consists only of monomer, initiator and solvent.

The monomer conversion, $X_1$ is defined in Table III. Defining the volume contraction parameter, $\varepsilon$, as
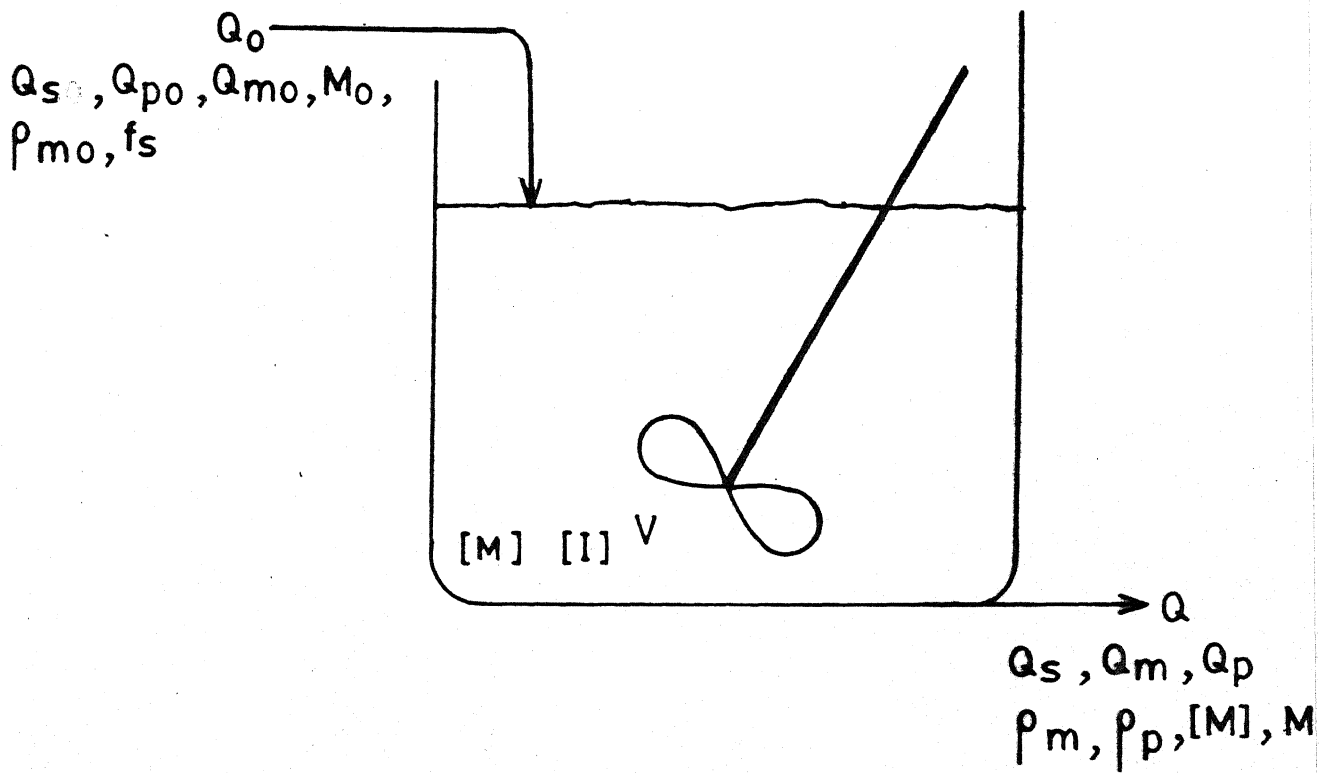
Figure 2 :  Schematic presentation of the continuous
flow stirred tank reactor (CSTR).

## TABLE II

### SPECIES BALANCE EQUATIONS FOR A CSTR [Fig.2]

Monomer Balance:

$$Q_o [M]_o - Q[M] = k_p \lambda_o [M] V \qquad (a)$$

Initiator Balance:

$$Q_o [I]_o - Q[I] = k_d [I] V \qquad (b)$$

Live Radical Balance:

n = 1 :

$$Q [P_1] = (2f k_d [I] - k_t [P_1] \lambda_o \qquad (c)$$

$$- k_p [P_1][M] ) V$$

n ⩾ 2 :

$$Q [P_n] = ( k_p [M] ( [P_{n-1}] - [P_n] )$$

$$- k_t [P_n ]\lambda_o ) V \qquad (d)$$

Energy Balance:

$$Q_o \rho_{mo} C_P (T_f - T) + (-\Delta H_r) k_p [M]\lambda_o V - hA (T-T_c) = 0$$

$$(e)$$

$$\varepsilon = \frac{\rho_p - \rho_m}{\rho_m} \qquad (3)$$

and with the help of Eqns.(2) and (3) Eqn. (1) can be simplified as,

$$Q = \frac{Q_o}{(1+\varepsilon)} \left[ \frac{(1-\varepsilon X_1)\,\rho_{mo}}{\rho_m} + \varepsilon \right] \qquad (4)$$

The various model equations of Table II can be made dimensionless with the help of Eqn. (4). They are presented in Table III. The various dimensionless variables and parameters are also defined there.

For the live radical balance, the quasi-steady state approximation (QSSA) can be taken for the live polymer. Although QSSA for live polymer fails at high conversion for nonisothermal batch reactors, several researchers have used the same for free radical solution polymerization in CSTRs[31,33], without much error. Thus equation (d) of Table III reduces to

$$\lambda_o^2 = \frac{2f\,k_d\,[I]_o\,(1-X_2)}{s\,k_t} \qquad (5)$$

Equations (a), (b) of Table III and Eqn. (5) can be combined into a single equation,

$$F(X_1, Da, \alpha, \beta, \delta) \triangleq \frac{2f\,[I]_o\,Da^2\,k_p^2\,k_d}{k(T_f)^2\,k_t} - \frac{s^2\,X_1^2}{(1-X_1)^2} \cdot$$

$$\left[ S + \frac{k_d}{k(T_f)}\,Da \right] = 0 \qquad (6)$$

## TABLE III

SPECIES BALANCE EQUATIONS IN DIMENSIONLESS FORM

Monomer Balance:

$$-X_1 + \frac{k_p \lambda_o}{k(T_f)} \frac{(1-X_1) \, Da}{S} = 0 \tag{a}$$

Initiator Balance:

$$-X_2 + \frac{k_d \cdot Da}{k(T_f)} \frac{(1-X_2)}{S} = 0 \tag{b}$$

Energy Balance:

$$-X_3 + Da \frac{(1-X_1)}{S} \cdot \frac{k_p \lambda_o}{k(T_f)} - Da(X_3 - \delta) = 0 \tag{c}$$

Live Radical Balance:

$$k_t \lambda_o^2 = \frac{2f \, k_d \, [I]_o \, (1-X_2)}{S} - \left[ \frac{(1-\epsilon X_1) \, \rho_{mo}}{\rho_m} + \epsilon \right]$$

$$\frac{\lambda_o}{(1+\epsilon) \, Da} \tag{d}$$

TABLE III (CONTD.)

where

$$X_1 = \frac{Q_o[M]_o - Q[M]}{Q_o[M]_o} = \frac{M_o - M}{M_o}$$

$$X_2 = \frac{Q_o[I]_o - Q[I]}{Q_o[I]_o}$$

$$X_3 = \frac{T - T_f}{T_f}$$

$$\alpha = \frac{hA}{\rho_{mo} C_P k(T_f) V} \qquad \beta = \frac{(-\Delta H_r)[M]_o}{\rho_{mo} C_P T_f}$$

$$\delta = \frac{T_c - T_f}{T_f} \qquad \tau = \frac{V}{Q_o}$$

$$E = E_p + (E_d - E_t)/2$$

$$k(T_f) = k_{p_o}^o \exp(-E/RT_f) \left(\frac{2f k_d^o [I]_o}{k_{t_o}^o}\right)^{\frac{1}{2}}$$

$$S = \left[\frac{(1-X_1)\rho_{mo}}{\rho_m} + \xi\right] / (1+\xi)$$

$$\xi = f_s/(1-f_s)$$

In order to obtain the relation between $X_3$ and $X_1$ in Table III, equation (a) is multiplied by $\beta$ and then subtracted from equation (c), giving,

$$X_3 = \frac{\beta X_1}{1 + \alpha Da} + \frac{\alpha Da}{1 + \alpha Da} \qquad (7)$$

For isothermal batch reactor simulation, mass balance equations relevant to the kinetic scheme of Table I, are presented in Table IV, using the present set of variables.

The constitutive equations for the gel and glass effect models of Chiu et al.[13] and Ross and Laurence[5] are shown in Table V. While the Ross and Laurence[5] model shows a discontinuity in the value of $k_t$ and $k_p$ at the onset of the gel and glass effects respectively, the model of Chiu et al.[13] gives $k_t$ and $k_p$ in the form of continuous functions, and hence these are easy to handle. Termination and propagation rate constants in the absence of the gel and glass effects predictably bear exponential relations to the reactor temperature, T. $\theta_t$ and $\theta_p$ also vary exponentially with temperature. Although $\theta_p$ does not vary with $[I]_o$, $\theta_t$ is indeed a function of $[I]_o$[13] (discussed later). These functional relationships are also presented in Table V.

Eqn. (6) defines a surface in the parameter space defined as

$$\underset{\sim}{p}^* = (\alpha, \beta, A, B, \varepsilon) \qquad (8)$$

## TABLE IV

SPECIES BALANCE EQUATIONS FOR ISOTHERMAL BATCH REACTOR

Monomer Balance:

$$\frac{dX_1}{dt} = k_p \, (1-X_1) \, \lambda_o \qquad\qquad (a)$$

Initiator Balance:

$$\frac{d[I]}{dt} = - k_d [I] + \frac{\epsilon [I]}{1- \epsilon X_1} \, \lambda_o \, (1-X_1) \, k_p \qquad (b)$$

Live Radical Balance:

$$\frac{d\lambda_o}{dt} = \frac{\epsilon \, \lambda_o^2}{1- \epsilon X_1} \, (1-X_1) \, k_p + 2f \, k_d \, [I] - k_t \, \lambda_o^2 \qquad (c)$$

## TABLE V

### CONSTITUTIVE GEL AND GLASS EFFECT EQUATIONS

**Ross and Laurence Model[5]:**

Gel Effect:

$$\frac{k_t}{k_{to}} = 0.10575 \exp\left[\, 17.15\, V_f - .01715\right.$$

$$\left. (T - 273.2)\,\right] \text{ for } V_f > 0.152$$

$$= 0.23 \times 10^{-5} \exp(75\, V_f) \text{ for } V_f \leq 0.152$$

Glass Effect:

$$\frac{k_p}{k_{po}} = 1.0 \text{ for } V_f \ngtr 0.05$$

$$= 0.71 \times 10^{-4} \exp\left[\, 171.53\, V_f\right]$$

where $V_f = 0.025 + \alpha_m (T - T_m) + [\alpha_p (T - T_p)$

$$- \alpha_m (T - T_m)]\, \phi_p$$

**Model of Chiu et al.[13]:**

Gel Effect:

$$\frac{k_t}{k_{to}} = \frac{1}{1 + \dfrac{\theta_t\, k_{to}\, \lambda_o}{C}}$$

Glass Effect:

$$\frac{k_p}{k_{po}} = \frac{1}{1 + \dfrac{\theta_p\, k_{po}\, \lambda_o}{C}}$$

TABLE V (CONTINUED)

where,

$$C = \exp \left[ \frac{2.303 \, \emptyset_m}{A + B \, \emptyset_m} \right]$$

$$\Theta_p = \Theta_p^o \exp \left( \frac{E_{\Theta p}}{RT} \right)$$

$$\Theta_t = \Theta_t^o \exp \left( \frac{E_{\Theta t}}{RT} \right)$$

$$k_{p_o} = k_{p_o}^o \exp \left( -E_p/RT \right)$$

$$k_{t_o} = k_{t_o}^o \exp \left( -E_t/RT \right)$$

$$k_d = k_d^o \exp \left( -E_d/RT \right)$$

$$\emptyset_m = \frac{1 - X_1}{1 - X_1 + \varepsilon}$$

$$\emptyset_p = \frac{X_1 (1 - \varepsilon)}{1 - \varepsilon X_1 + \varepsilon}$$

and this surface is called the steady state manifold of the system. A bifurcation parameter is said to be the one which can give rise to transitions from unique to multiple solutions or vice versa in a plot of conversion vs. this parameter, for a given set of values of the other parameters. For example, dimensionless mean residence time, Da is usded as a bifurcation parameter in Figure 1. Plot (e) of Figure 1 exhibits four bifurcation points (transition point between uniqueness and multiplicity) in the transition scheme of 1-3-1-3-1 solutions. According to Golubitsky and Keyfitz[19], the surface in the parameter space, $\underset{\sim}{p}^*$ at which the continuous change of a parameter causes the appearance or disappearance of an S or inverse S pattern (Figure 1(a) and (b) respectively) is called the "hysteresis" variety. The following conditions are to be satisfied by the hysteresis variety[20]:

$$F ( X_1, Da, \underset{\sim}{p}^* ) = 0 \qquad (a)$$

$$\frac{\delta F}{\delta X_1} ( X_1, Da, \underset{\sim}{p}^* ) = 0 \qquad (b)$$

$$\frac{\delta^2 F}{\delta X_1^2} ( X_1, Da, \underset{\sim}{p}^* ) = 0 \qquad (c) \qquad (9)$$

Similarly, the isola variety defines a surface in the parameter space, $\underset{\sim}{p}^*$, where the continous change of one of the parameters causes the apprearance or disappearance of an isolated branch in the conversion vs. mean residence time plot, and satisfies

Eqns. (9a), (9b) and

$$\frac{\delta F}{\delta Da} (X_1, Da, \underset{\sim}{p}^*) = 0 \qquad\qquad (10)$$

Introduction of the influence of the gel effect on the propagation and termination rate constants makes the mass and energy balance equations very complex and consequently eqn. 6. For this reason, it is extremely difficult to eliminate Da from eqns. (9a) – (9c) to get an explicit relation between $\alpha$ and $\beta$ for the generation of an $\alpha - \beta$ plot. Function F, in eqn. (6) is differentiated twice with respect to $X_1$ to give three non-linear algebraic equations in $X_1$, $\alpha$, $\beta$, Da and $\delta$, which can be solved simultaneously with the NAG subroutine C05NBF to give values of $X_1$, $\alpha$ and $\beta$ Da for given values of $\beta$ and $\delta$. This gives the $\alpha$–$\beta$ plot for the hysterisis variety. Similarly, for the isola variety, function F is differentiated once with respect to Da and the resulting equation is solved simultaneously with eqns. (9a) and (9b) to give an $\alpha - \beta$ plot for the isola variety for a given value of $\delta$. The whole $\alpha$–$\beta$ plot thus generated is shown to be divided into various regions, each representing different multiplicity patterns of the conversion versus time plot. Particularly, the whole $\alpha$–$\beta$ plot has been divided into five major domains. Each type of multiplicity pattern can be verified by picking up parameter values from that region and generating the conversion vs. Da plot. For batch

reactor simulation and for the study of steady state

multiplicity of CSTRs, PMMA polymerization in CSTRs is

taken as an example and the various physical properties

and parameter values for this system are presented in

Table VI.

## TABLE VI

### VALUES OF PARAMETERS FOR PMMA[14,31,32]

$f$ = 0.58 (AIBN)

$A$ = $0.168 - 8.17 \times 10^{-6} (T-387)^2$ (Ref.13)

$B$ = 0.03 (Ref.13)

$C_p$ = 0.4 cal/g °C

$\rho_m$ = $0.973 - 0.001164 (T-273)$ g/cm$^3$ (Ref.13)

$\rho_p$ = 1.2 g/cm$^3$ (Ref.13)

$E_d$ = 30.66 kcal/mol (Ref.13)

$E_p$ = 4.35 kcal/mol (Ref.13)

$E_t$ = 0.701 kcal/mol (Ref.13)

$E_{\theta p}$ = 27.82 kcal/mol

$E_{\theta t}$ = 34.176 kcal/mol

$(-\Delta H_r)$= 13.5 kcal/mol (Ref.35)

$k_d^o$ = $6.32 \times 10^{16}$ min$^{-1}$ (Ref.13)

$k_{p_o}^o$ = $2.95 \times 10^7$ lit/mol-min

$k_{t_o}^o$ = $5.88 \times 10^9$ lit/mol-min

$\theta_p^o$ = $5.48 \times 10^{-16}$ min

$\theta_t^o$ = $3.372 \times 10^{-22}$ mol-min/lit

$\varepsilon$ = $\dfrac{\rho_p - \rho_m}{\rho_p} = 0.1946 + 0.916 \times 10^{-3} (T-273)$ (Ref.13)

$\alpha_p$ = 0.00048 (Ref.5)

$\alpha_m$ = 0.001 (Ref.5)

$T_p$ = 387.0 (Ref.5)

$T_m$ = 167.0 (Ref.5)

CHAPTER III

RESULTS AND DISCUSSION

It has been mentioned earlier, that we have used the gel effect models of Chiu et al.[13] and Ross and Laurence[5], in our work. Results using the correlation of Chiu et al.[13] are presented first. A careful survey of the various publications of Soong and coworkers[13,36-39,41] reveals that they have used different values for the parameters $\theta_t^o$, $\theta_p^o$, $E_{\theta_t}$ and $E_{\theta_p}$ in their correlations for $\theta_t$ and $\theta_p$ (Table V). Chiu et al.[13] had matched experimental conversion – time data on batch reactors of Marten and Hamielec[7] at three temperatures, 50°C, 70°C and 90°C quite well, using values of $\theta_p$ and $\theta_t$ shown in Table VII. The agreement at one temperature, namely at 90°C for two different values of $[I]_o$ is shown in Figure 3 (curves a) Chiu et al.[13] tried to correlate the three sets of values of $\theta_p$ and $\theta_t$ given in Table VII with the exponential relationships:

$$\theta_p = \theta_p^o \exp ( E_{\theta_p} /RT) \qquad \text{(a)}$$

$$\theta_t = \frac{\theta_t^o}{[I]_o} \exp ( E_{\theta_t} /RT) \qquad \text{(b)} \qquad \text{(11)}$$

## TABLE VII

$\Theta_t$ and $\Theta_p$ Values Used by Chiu et al.[13] in Fitting
Experimental Data of Marten-Hamielec[7].

| Initiator loading, $[I]_o$ mol/l | Polymerization Temperature, t°C | $\Theta_t$, min | $\Theta_p$, min |
|---|---|---|---|
| 0.0258 | 50 | 1500.00 | 3500.00 |
| | 70 | 49.00 | 250.00 |
| | 90 | 3.80 | 30.00 |
| 0.01548 | 50 | 2330.00 | 3500.00 |
| | 70 | 83.00 | 250.00 |
| | 90 | 6.30 | 30.00 |
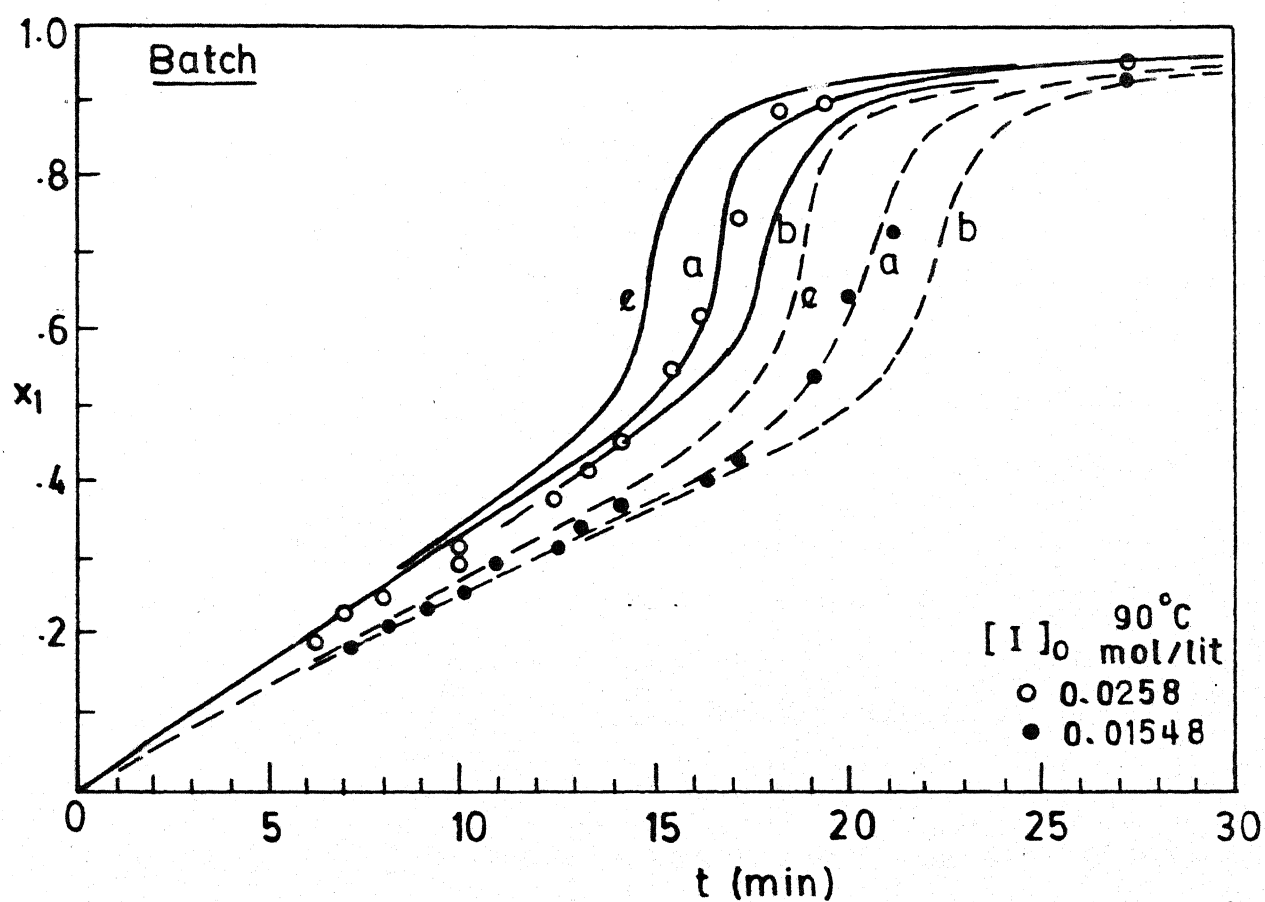
Figure 3 : Comparison of batch reactor simulation
results for PMMA polymerization using parameter
values $\theta_t^o$, $\theta_p^o$, $E_{\theta_t}$ and $E_{\theta_p}$ from Table VIII
(column b) with experimental data(o,●)at 90°C

Thus, plots of ln $(1/\theta)$ vs. $1/T$ would be straight lines,

which would give the values of the parameters $\theta_t^o$, $\theta_p^o$,

$E_{\theta_t}$ and $E_{\theta_{pi}}$. Their values are reported in Table VIII in

column (b)[41]. When these values of the parameters are

used at 50°C, 70°C and 90°C, it is observed that the

calculated values of $\theta_t$ and $\theta_p$ are quite different from

those given in Table VII. A comparison at 90°C is also

shown in Table VIII. Obviously, conversion - time plots

do not match experimental isothermal batch reactor data

at different temperatures, as shown in Figure 3 (curves b)

for 90°C. Louie at al.[37] used values of the four parameters

$\theta_t^o$, $\theta_p^o$, $E_{\theta_t}$, and $E_{\theta_p}$ as given in column d, Table VIII.

Using these values it is observed from Figure 4 (curves d)

that the conversion vs. time plots at constant temperature

again do not match experimental results too well. Another set of

parameter values were obtained by Kapur at al.[40] (Column c,

Table VIII) to match nonisothermal plug-flow reactor simulation

results of Baillagou and Soong[36,38]. The corresponding

results for isothermal batch reactor polymerization at 90°C

are shown as curve c in Figure 4. Poor agreement with

experimental results is once again observed. In the present

work, we have used the values shown in column e, Table VIII,

since these match constant temperature simulation results

of Carrat et al.[41] on CSTRs. The values shown in column b,

Table VIII fail to duplicate the results in Ref. 41.

## TABLE VIII

Comparison of the Values of the Parameters $\theta_t^o$, $\theta_p^o$, $E_{\theta_t}$ and $E_{\theta_p}$
Used by Various Workers[13,36-39,41]

| Parameters | Curves a | b | c | d | e |
|---|---|---|---|---|---|
| $\theta_p^o$ | — | $5.48 \times 10^{-16}$ | $5.4814 \times 10^{-16}$ | $5.4814 \times 10^{-16}$ | $5.48 \times 10^{-16}$ |
| $\theta_t^o$ | — | $1.14 \times 10^{-22}$ | $1.1553 \times 10^{-22}$ | $1.1353 \times 10^{-22}$ | $3.372 \times 10^{-22}$ |
| $E_{\theta_t}/R$ | — | 17400 | 17200 | 17420 | 17200 |
| $E_{\theta_p}/R$ | — | 14000 | 14100 | 13982 | 14000 |
| $\theta_t$ ( at 90°C, $[I]_o = 0.0258$ mol/l ) | 3.80 | 2.9021 | 1.695 | 3.0538 | 4.9478 |
| $\theta_t$ (at 90°C, $[I]_o = 0.01548$ mol/l ) | 6.30 | 4.836 | 2.8253 | 5.09 | 8.2462 |
| $\theta_p$ (90°C) | 30.00 | 30.79142 | 40.567 | 29.31 | 30.7914 |
| Ref No. | 13 | 41 | 40 | 37 | Present work |
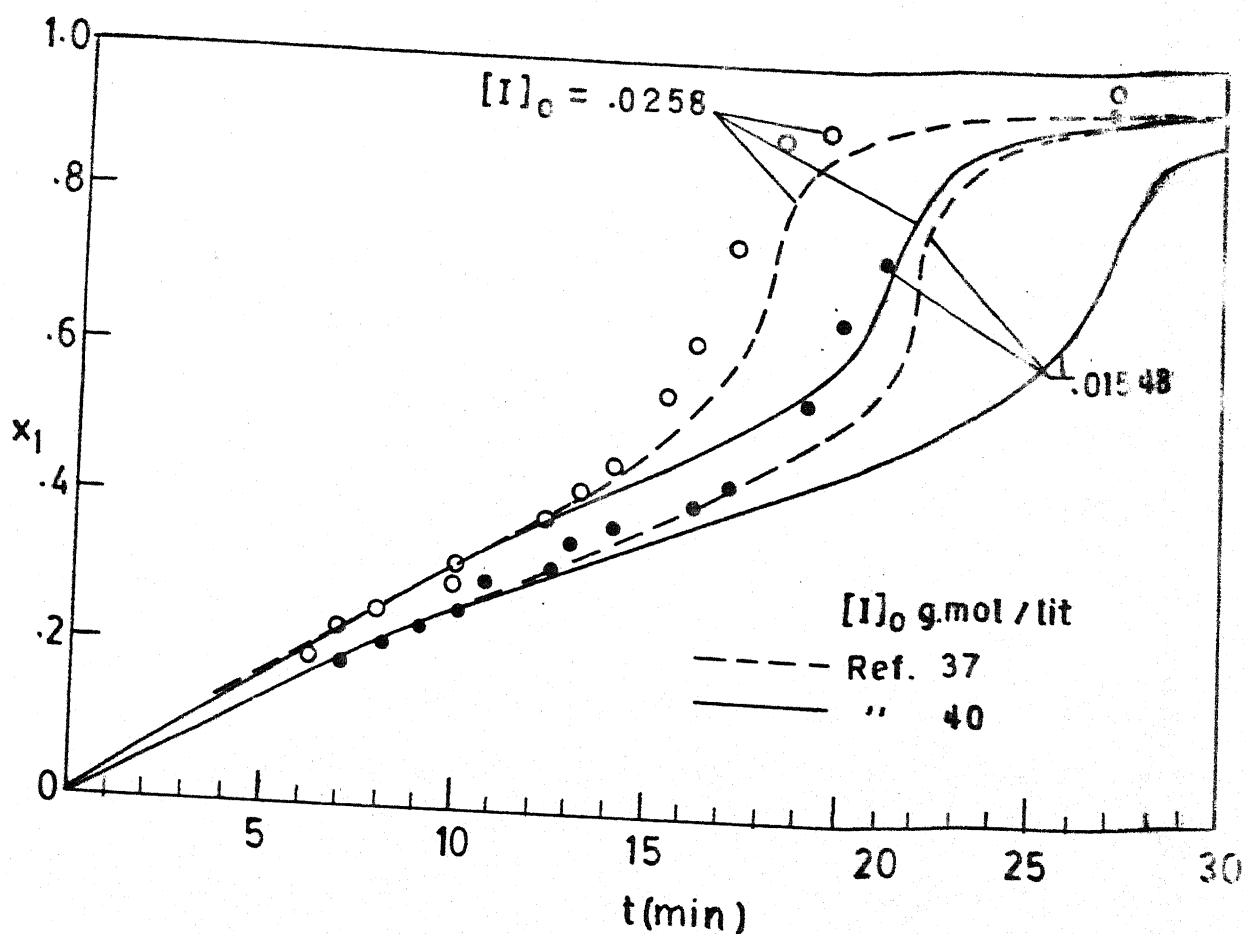
Figure 4 : Comparison of batch reactor simulation
results for PMMA polymerization using
parameters $\theta_t^o$, $\theta_p^o$, $E_{\theta_t}$ and $E_{\theta_p}$ from Table VIII
(column c and d) with experimental data (o, ●)
at 90°C

Figure 3 (curves e) shows that this choice of parameters again leads to poor agreement with isothermal batch reactor data.

CSTR simulation results have been generated using the parameter values of column e, Table VIII, at constant temperatures of 50°C, 60°C, 70°C, 80°C and 90°C. These are shown in Figure 5. Also shown in this figure are the simulation results of Carrat et al.[41] using, the parameter values in column b, Table VIII. There is some difference observed between the two sets of results, particularly at low temperatures, but this was the best agreement we could obtain without using an elaborate optimization algorithm for obtaining the parameters. These parameters (Column e, Table VIII) have been used finally to study multiplicity of steady state in CSTRs.

Figure 6 shows some constant temperature simulation results on CSTRs using the parameters in columns a and e in Table VIII. Considerable disagreement exists, particularly at the lower temperatures between these results. It is known that $\theta_t$ is a function of the molecular weight. This, in turn, is a function of the initiator concentration in the reactor. Chiu et al.[13], used $\theta_t$ as a function of $[I]_o$ the initiator concentration in the feed (to the batch reactor). However, we replaced this by $\theta_t = \theta_t([I])$, and accordingly,

generated simulation results on CSTRs. These are shown
in Figure 7. We observed that this does not lead to very
different results compared to when $[I]_o$ was used, and
so to use the latter for multiplicity studies.

In summary, we observe that there is quite a
confusion regarding the parameter values for $\Theta_p$ and $\Theta_t$
in the literature, and even the same group of workers have
used different parameter values in different publications.
Our own set e (Table VIII) was thus used for multiplicity
studies since this gave simulation results on constant
temperature CSTRs, matching those of Carrat et al.[41].

Along with Chiu et al.'s[13] model, the model of Ross
and Laurence[5] for the gel and glass effects is studied
extensively to predict its applicability for free radical
polymerization in batch reactors

and CSTRs. For PMMA polymerization,
values of the various parameters in the model of Ross and
Laurence are shown in Table IV and the model is presented
in Table V. The Model of Ross and Laurence[5] for $k_t/k_{t,o}$ and
$k_p/k_{po}$ is used along with the $k_{to}$, $k_{po}$ values of Chiu et al.[13]
to generate batch reactor simulation results. These are
shown in Figure 9. Results for varying initiator efficiency,
f, as well as a constant f of 0.58 are shown. The results
using variable f are close to the experimental data.
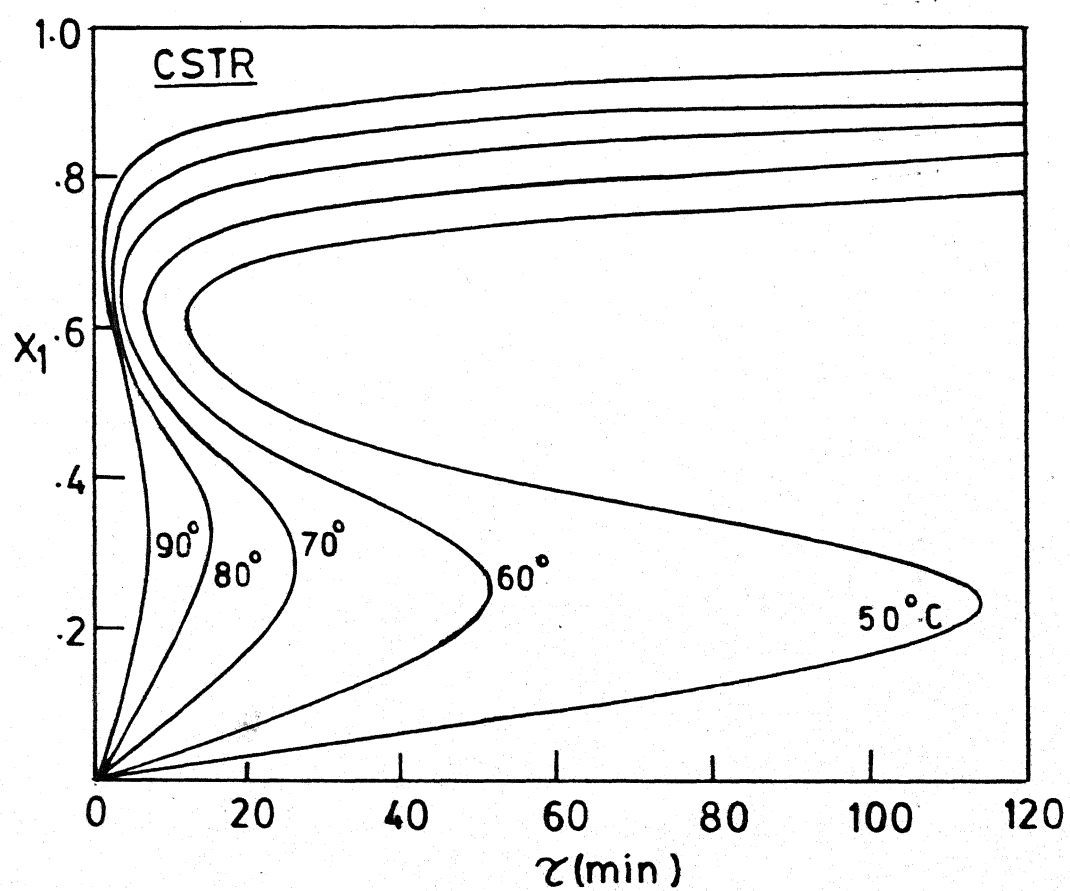
Figure 5 : CSTR simulation results with parameters $\Theta_t^O$, $\Theta_p^O$, $E_{\Theta_t}$ and $E_{\Theta_p}$ from Table VIII (column e)
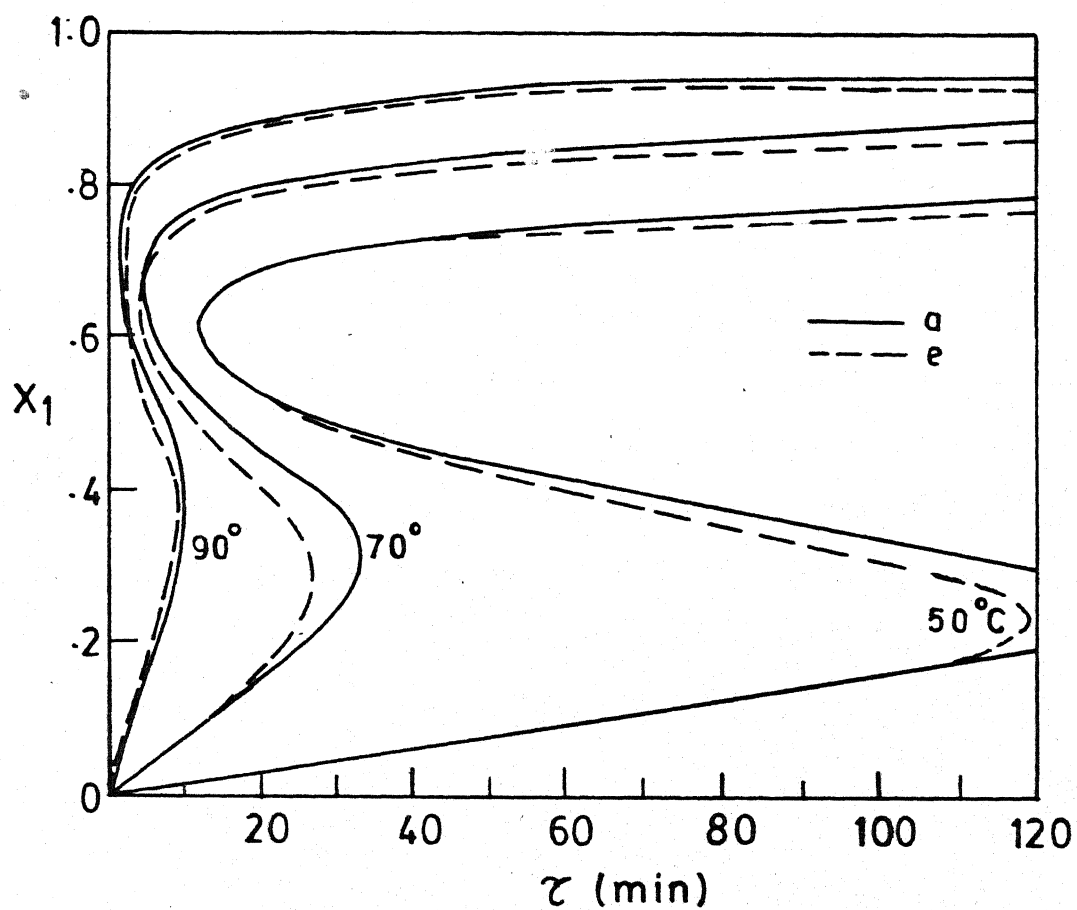
Figure 6 : CSTR simulation results using parameters, $\theta_t^o$, $\theta_p^o$, $E_{\theta_t}$ and $E_{\theta_p}$ from Table VIII (column a and e)

CSTR simulation results are generated for constant f, using the Ross and Laurence equations for the gel and glass effects. These are plotted in Figure 10. The Ross and Laurenace[5] plots show two discontinuities in each of the curves, one at the onset of the gel effect and the other at the onset of the glass effect. These are associated with the use of different equations for the gel and glass effects in Table V before and after a critical value of the free volume. The results using the parameter values of Table VIII (column e) at 50°C, 70°C and 90°C are also shown in Figure 10 for comparison. Although they match well at 90°C, for other temperatures they do not match. Obviously multiplicity features are expected to differ significantly for the two models. In this work, we have used the Chiu et al.[13] model for the gel and glass effects with parameter values as in column e of Table VIII to study multiplicity of steady states in CSTRs.

Choi[35] studied the steady state multiplicity patterns of CSTRs without the gel effect, considering free radical solution polymerization of PMMA with fs > 0.6, and generated an $\alpha-\rho$ plot to depict the regions of various multiplicity patterns following the technique of Balakotaiah and Luss[20]. However, he did not consider, in his methodology, the change in initiator concentration due to reaction, i.e., $[I] = [I]_0$. In the present study, the change in the initiator concentration
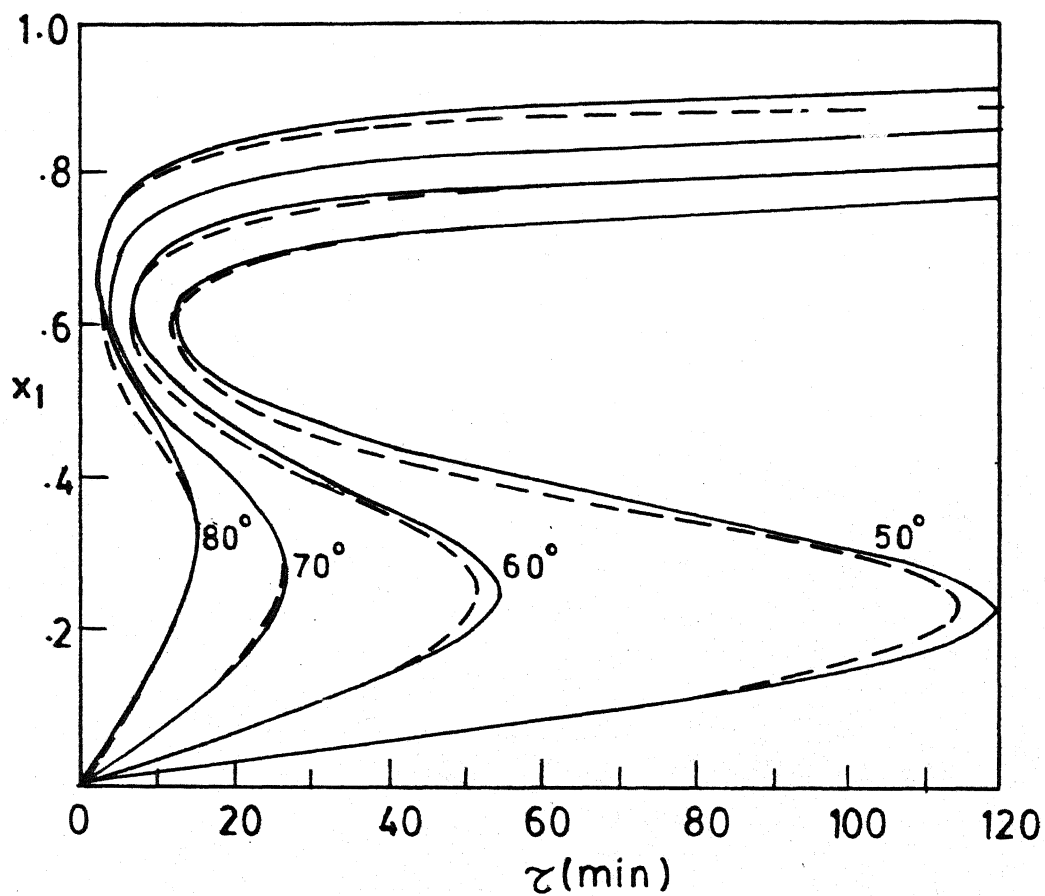
Figure 7 : CSTR simulation results with parameters $\Theta_t^o$, $\Theta_p^o$, $E_{\Theta_t}$ and $E_{\Theta_p}$ from Table VIII (column e)

····· for $\Theta_t = \Theta_t (\lceil I \rceil)$

——— for $\Theta_t = \Theta_t (\lceil I \rceil_o)$
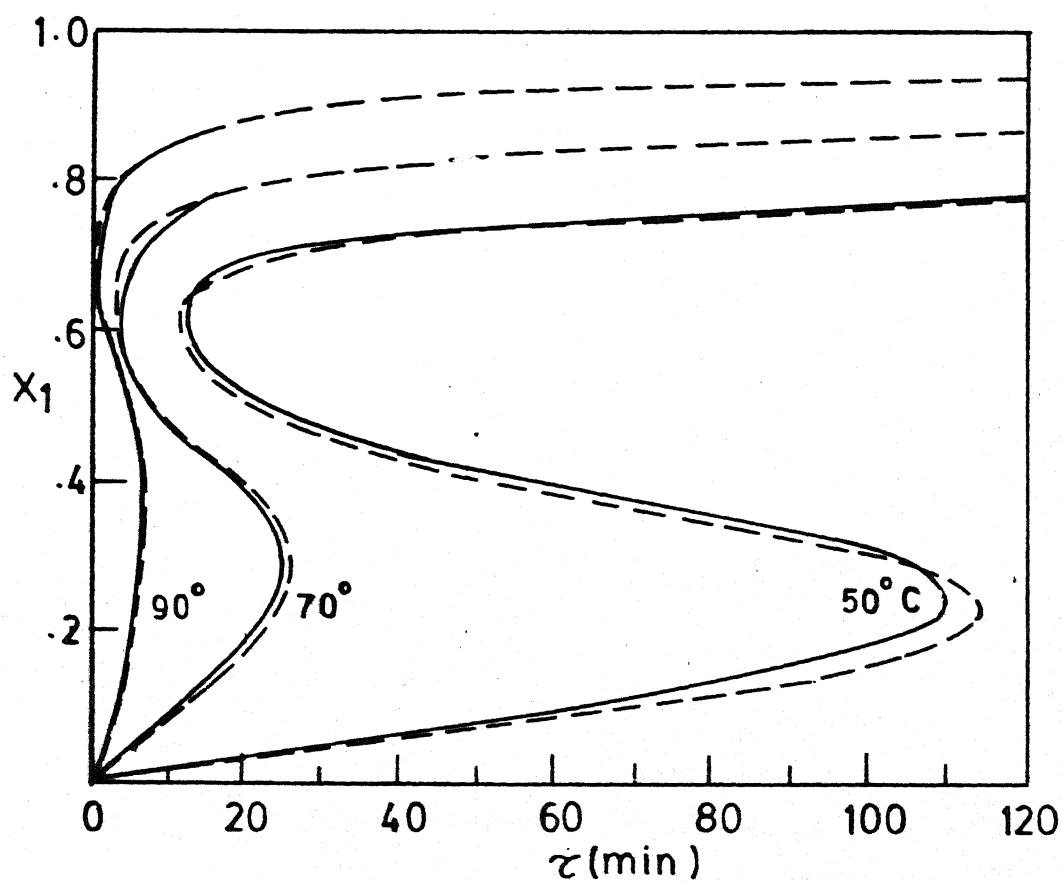
Figure 8 :    Comparison of CSTR simulation results with

parameters  $\Theta_t^0$,  $\Theta_p^0$,  $E_{\Theta_t}$  and  $E_{\Theta_p}$  from

Table VIII (column e) with the results

reporduced from Carrat et al.'s[41]  plot.
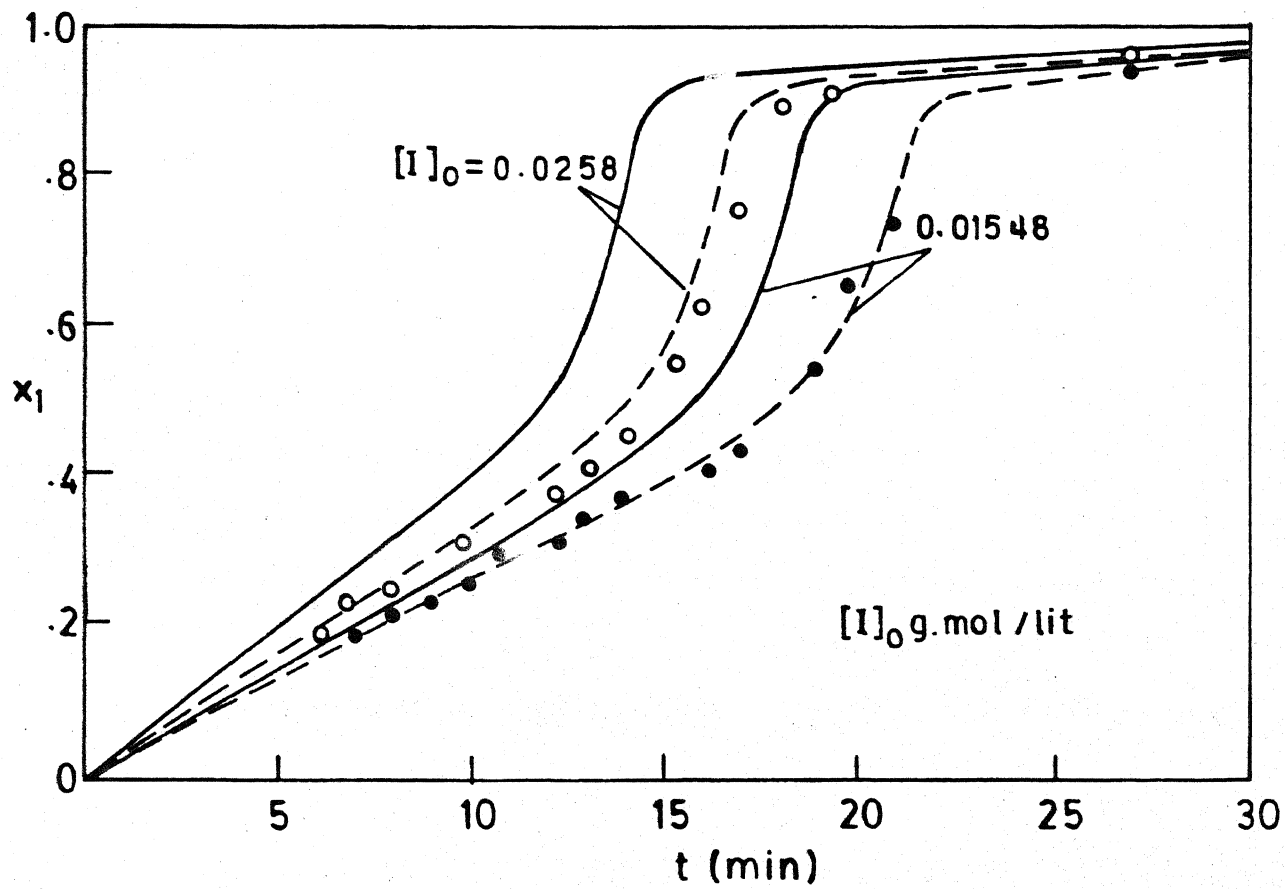
Figure 9 : Batch reactor simulation results using Ross and Laurence gel effect model. Results for varying, f = 0.487-2.51 (dotted line) and f = 0.58 are presented (solid line)

has been taken into account. Figure 11 shows the $\alpha-\beta$ plot

for the hysteresis and isola varieties. In this figure,

curve a shows the results of Choi[35] for the hysteresis

variety in the absence of the gel effect. The rate

constants are different than those given in Table VI.

and are:

$$k_d = 3.57 \times 10^{15} \, e^{-29600/RT} \, min^{-1}$$

$$k_{po} = 4.2 \times 10^{8} \, e^{-6300/RT} \, lit/(mol-min)$$

$$k_{t,o} = 2.112 \times 10^{11} \, e^{-2800/RT} \, lit/(mol-min) \qquad (11)$$

Curve b shows the hysteresis variety using the rate constants

(in absence of the gel effect) of Chiu et al.[13], as given

in Table VI. In addition, the assumption $[I] = [I]_o$ is

not used, nor are density changes accounted for. Similarly

curves c and d give the corresponding isola variety plots

for the same situations.

Simulation results for CSTRs for some values of $\alpha$

and $\beta$ in different regions of Figure 11 are shown (Fig. 12) using

the rate constants (in absence of gel effect) of Table VI

and not using $[I] = [I]_o$. Uniqueness, hysteresis as

well as isolas are observed under appropriate conditions.

The last part of the present work is devoted to

the study of steady state multiplity with the gel and

glass effects for PMMA polymerization. The functions F,
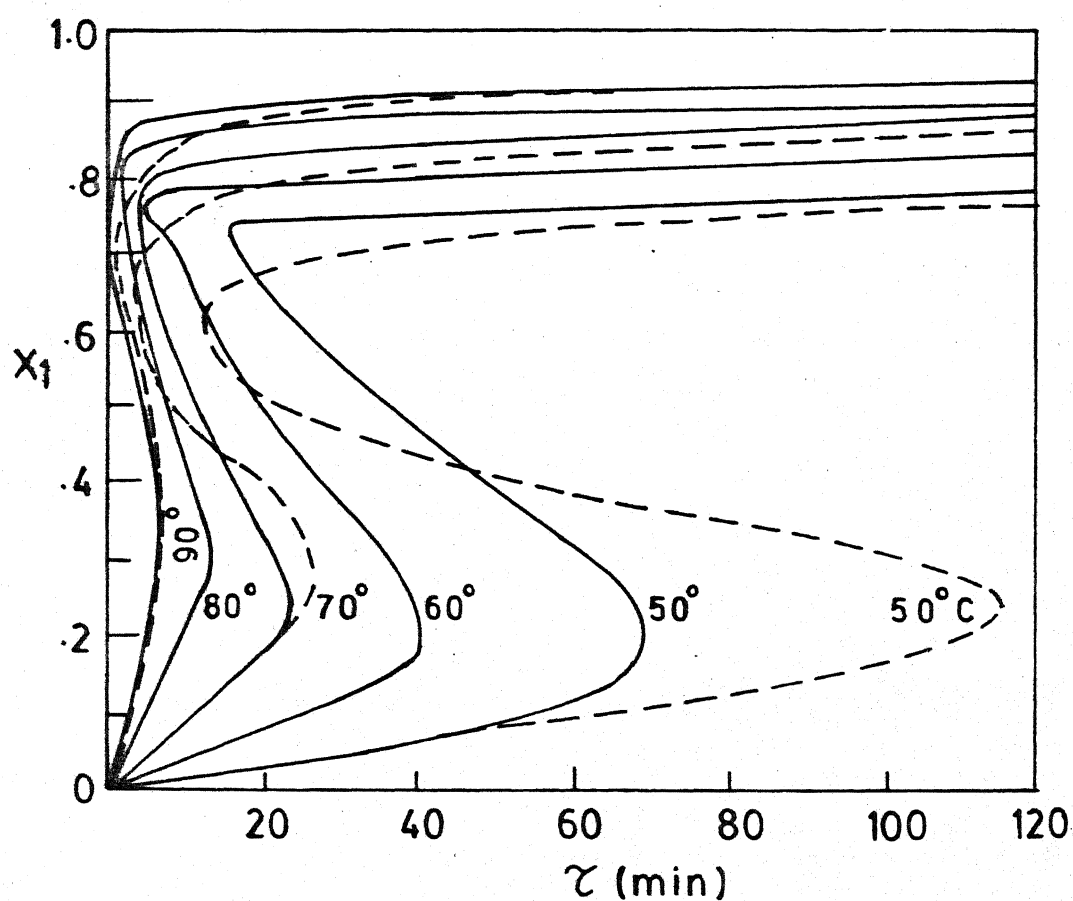
Figure 10 :  Comparison of CSTR simulation results using

Ross and Laurence gel effect model with

Chiu et al.'s model.  Parameters $\theta_t^o$, $\theta_p^o$,

$E_{\theta_t}$ and $E_{\theta_p}$ are taken from Table VIII

(column e), f = 0.58

$F_{X_1}$, $F_{X_1 X_1}$ and $F_{Da}$ are so stiff that simultaneous solution of the two sets of eqns. (9a)-(9c) and (9a), (9b) and 10 is very difficult. These simultaneous equations are very sensitive to changes in the initial guesses using the NAG subroutine C05NBF. For this reason and for lack of time, an attempt has been made to obtain an approximate $\alpha - \beta$ plot from simulation results, rather than from the technique of Balakotaiah and Luss[20]. These results are shown in Figure 13. Simulation results taking some of the parameter values from Figure 13 are presented in Figure 14. These plots have been generated using data in Table VI and column e of Table VIII. It is hoped that precise boundaries in the $\alpha - \beta$ plot in the presence of the gel effect will be obtained in the near future.
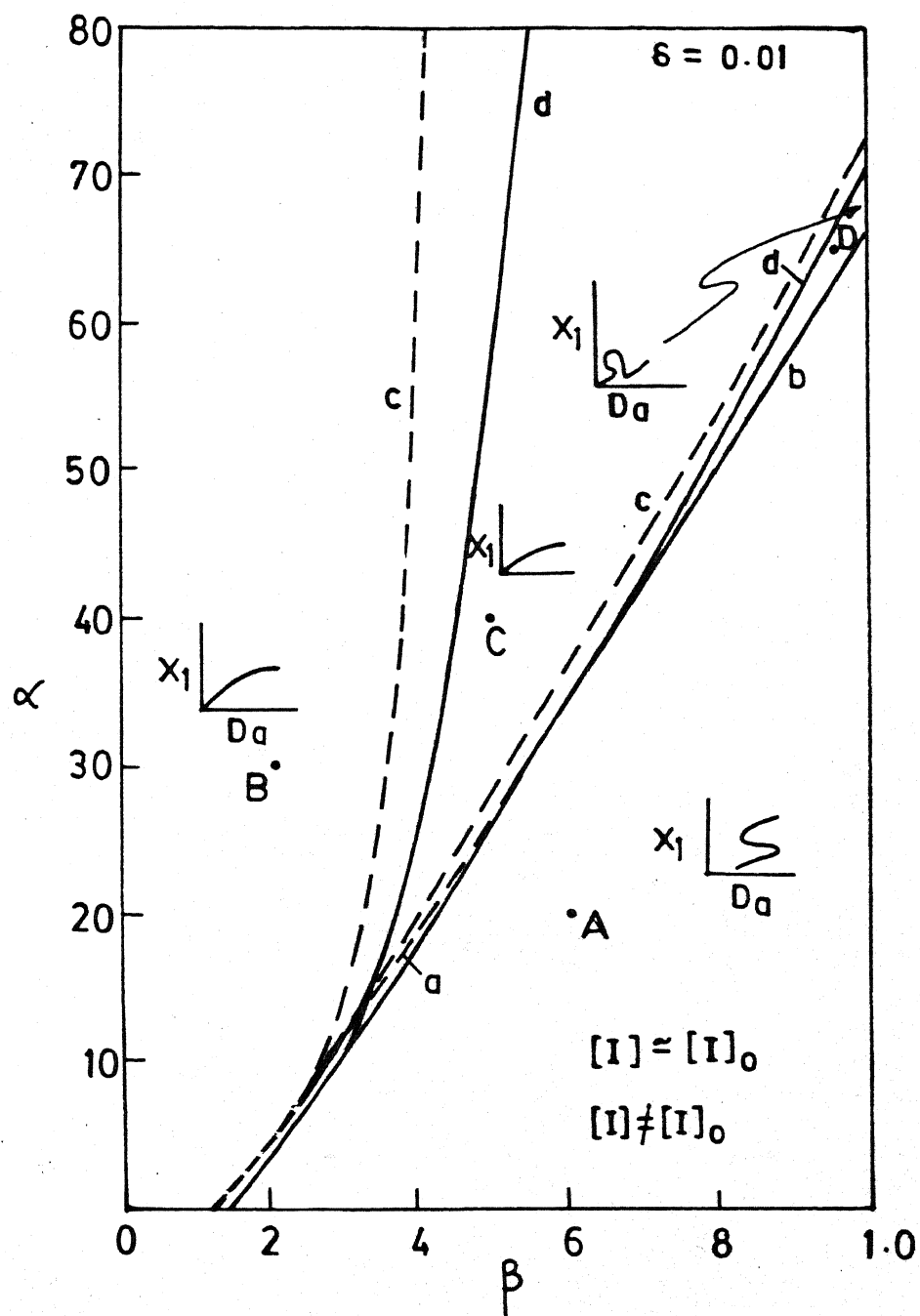
Figure 11 : Bifurcation behaviour of CSTRs for solution
polymerization of PMMA without gel effect.
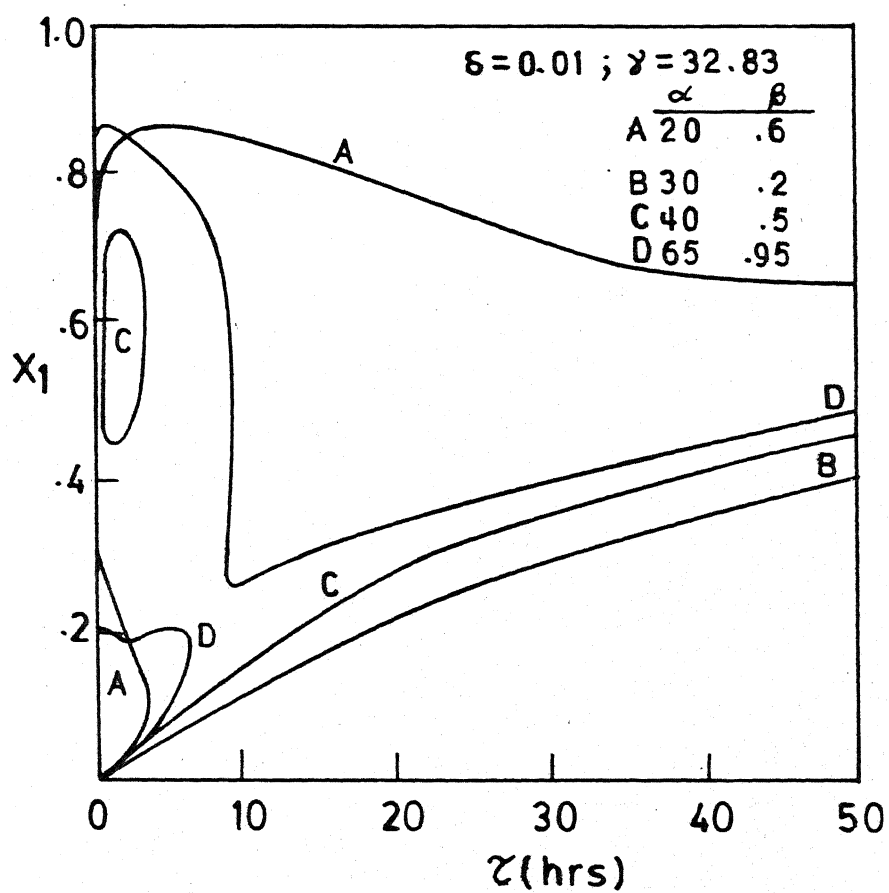
Figure 12 : CSTR simulation results for free radical
solution polymerization of PMMA using
different values of the parameters $\alpha$ and $\beta$
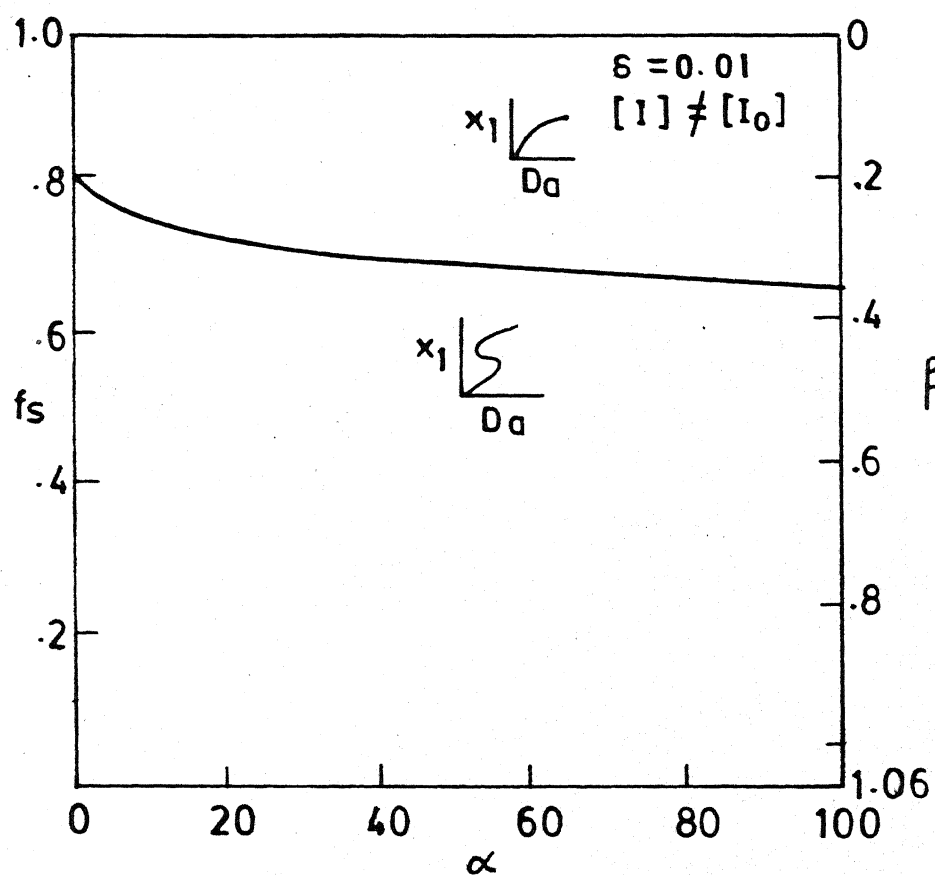
Figure 13 : Bifurcation behaviour of CSTRs for solution
polymerization of PMMA with gel effect.
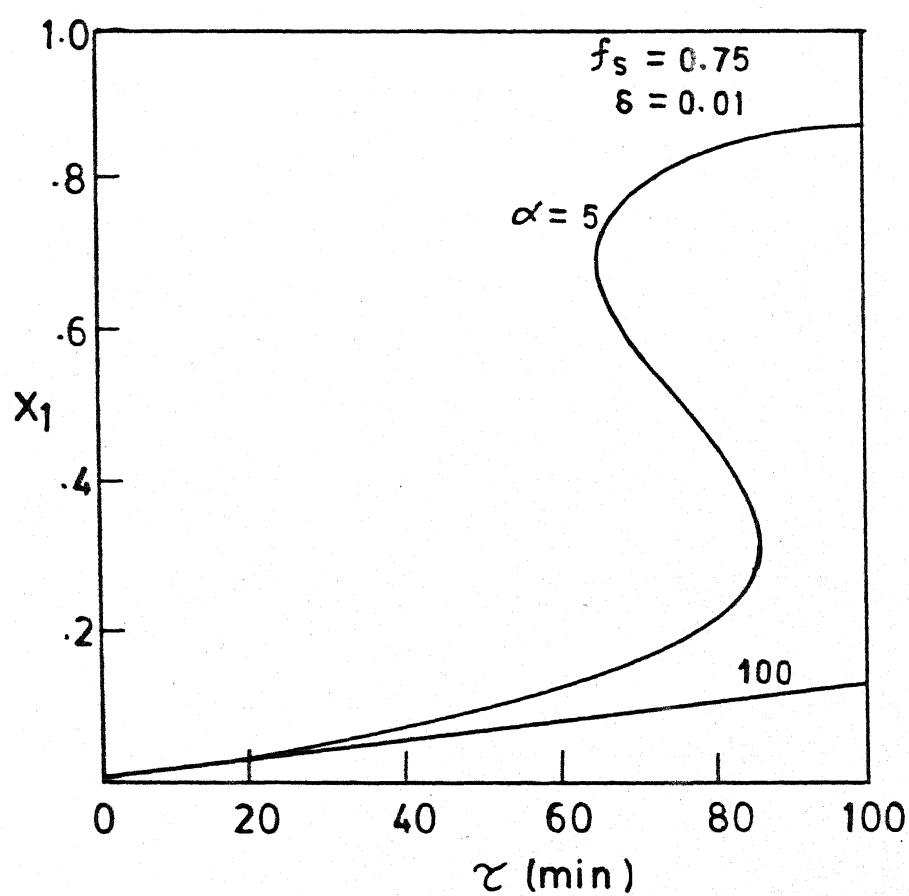
Figure 14 : Simulation results with gel effect for
solution polymerization of PMMA in CSTRs
using different values of α and β .

# CONCLUSION

Modified parameter values for the gel effect
equations of Chiu et al. give closest match to the
CSTR simulation results of Carrat et al. and can be
used for the study of steady state multiplicity of
CSTRs with gel effect. Although only two types of steady
state patterns are obtained from the simulation results for
the case with gel effect a specific bifurcation diagram
is needed for the possibility of other types of steady
state patterns in this case. A knowledge of stability
of these multiple solutions may help efficient control
of the reactor.

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C   PMMA POYMERIZATION IN CSTR  : SIMULATION
C
C   DEFINITION OF VARIABLES
C   A , B    =   PARAMETER OF THE    FUJITA - DOLITTLE CORRELATION
C                FOR  (D/DO).
C   ALPHA    =   HEAT TRANSFER PARAMETER
C   BETA     =   HEAT GENERATION PARAMETER
C   DELTA    =   DIMENSIONLESS COOLANT TEMPERATURE
C            =   D/DO
C   D/DO     =   RATIO OF DIFFUSIVITIES  WITH GEL EFFECT TO THAT
C                WITH  GEL EFFECT.
C   EFF      =   INITIATOR EFFICIENCY
C   EP       =   ACTIVATION ENERGY FOR PROPAGATION / R
C   ED       =   ACTIVATION ENERGY FOR INITIATOR DECOMP. / R
C   ET       =   ACTIVATION ENERGY FOR TERMINATION / R
C   FS       =   SOLVENT VOLUME FRACTION IN THE FEED.
C   INDEX2   =   PARAMETER INDICATING CHOI'S RATE CONSTANT FOR
C                INDEX2 = 1 AND  SOONG'S RATE CONSTANT FOR INDEX2==  = 2
C   IO       =   INITIATOR CONCENTRATION , GM - MOL/LIT
C   INDEX1   =   PARAMETER INDICATING GEL EFFECT FOR INDEX1 = 1 AND
C                ABSENCE OF GEL EFFECT FOR  INDEX1 = 2
C   KD       =   INITIATOR DECOMPOSITION RATE CONSTANT
C   KDO      =   PRE - EXPONENTIAL PART OF  KD
C   KT       =   TERMINATION RATE CONSTANT
C   KTO      =   TERMINATION RATE CONSTANT IN ABSENCE OF GEL EFFECT
C   KTOO     =   PRE - EXPONENTIAL PART OF KTO
C   KP       =   PROPAGATION RATE CONSTANT
C   KPO      =   PROPAGATION RATE CONSTANT IN ABSENCE OF GLASS EFFECT
C   KPOO     =   PRE - EXPONENTIAL PART OF KPO
C   LOO      =   LIVE RADICAL POPULATION
C   LOOKP    =   PRODUCT OF  LOO  AND  KP
C   T        =   TEMPERATURE IN  DEG. K.
C   TF       =   FEED TEMPERATURE
C   DA       =   DAMKOHLER  NUMBER
C   PHIM     =   MONOMER VOLUME FRACTION
C   ROM      =   DENSITY OF THE MONOMER AT THE REACTOR TEMPERATURE
C   ROMO     =   DENSITY OF THE MONOMER AT THE FEED TEMPERATURE
C   EPSS     =   VOLUME CONTRACTION PARAMETER , ( ROO - ROM)/ROO
C   F3       =   ROMO / ROM
C   DR       =   DENSITY RATIO , ROM/ROMO
C   X1       =   MONOMER CONVERSION
C   X3       =   DIMENSIONLESS TEMPERATURE
C   ----------------------------------------------------------------
      DIMENSION X(20)
      INTEGER ITMAX,IER,N,NSIG,INDEX1,INDEX2,INT
      COMMON ALPHA,BETA,TAU,INDEX1,INDEX2,FS, TF
      EXTERNAL FUN
      OPEN(UNIT=22,DEVICE='DSK',FILE='SIMS.OUT')
      OPEN(UNIT=6,DEVICE='DSK')
C   ================================================================
      WRITE(5,100)
      READ(5,*)INDEX1
      WRITE(5,101)
      READ(5,*) INDEX2
      INDEX1 = 2  ; INDEX2 = 2
C   OPERATING CONDITIONS
C
      FS = 0.6
C
      TF = 300.0  ; EMEM = 100.0 ; DELHR = 13.5 ; ROCP = 0.4
```

```
      ALPHA= 5000.0
      ROMO = 0.973 - 0.001164 * (TF -1273.0)
      EMEF = (1.0 -FS) * ROMO * 1000.0/EMEM
      BETA = DELHR * EMEF/(ROCP * TF) ; TYPE *,BETA

      WRITE(22,700) ALPHA,BETA
700   FORMAT(5X,'ALPHA =',F10.6,3X,'BETA=',E13.6/)
C     =================================================================
      N=6
      TAU=0
      IF(INDEX1.EQ.1) INT=100
      IF(INDEX1.EQ.2) INT = 150
      DO 102 M=1,INT
      TYPE 556
556   FORMAT(5X,'I AM HERE')
      X(1)=0.957
      X(2)=0.85
      X(3)=0.613
      X(4)=0.291
      X(5)=0.1
      X(6) = 0.05
      IF(INDEX1.EQ.1) TINC=30
      IF(INDEX1.EQ.2) TINC = 1
      TAU=TAU+TINC
      IF(INDEX1.EQ.1) TIME=TAU/60
      IF(INDEX1.EQ.1) TYPE 580,TIME
      IF(INDEX1.EQ.2) TIME=TAU
      IF(INDEX1.EQ.2) TYPE 581, TIME
581   FORMAT(5X,'TIME IN MINUTES = ',E13.6)
580   FORMAT(5X,'TIME  IN HOURS=',E13.6/)
C     =================================================================
      EPS=1.0E-7 ; EPS2=1.0E-6 ; ETA=0.000001 ; NSIG=6 ; ITMAX=30
C     =================================================================
      CALL ZREAL1(FUN,EPS,EPS2,ETA,NSIG,N,X,ITMAX,IER)
      CALL UERTST(IER,FUN)
      IF(INDEX1.EQ.1) WRITE(22,1501) TIME
      IF(INDEX1.EQ.2) WRITE(22,1502) TIME
1501  FORMAT(/5X,'** TIME IN HOURS=',E13.6/)
1502  FORMAT(5X,'** TIME IN MINUTES= ',E13.6/)
      DO 555 J=1,5
      IF(X(J).GT.1.0) GOTO 555
      IF(X(J).LT.0.0) GOTO 555
      X1 = X(J)
      TYPE 181, X1
      WRITE(22, 181) X1
181   FORMAT(5X,'SOLUTION = ',E13.6)
555   CONTINUE
      WRITE(22)
102   CONTINUE
100   FORMAT(5X,'TYPE IN THE VALUE OF INDEX1'/)
101   FORMAT(5X,'TYPE IN THE VALUE OF INDEX2'/)
      STOP
      END
C     =================================================================
      FUNCTION FUN(X1)
      INTEGER INDEX1,INDEX2
      REAL IO,KTO,KPO,KO,KP,KT,KPKPO,KTKTO,LDOKP,LDO
      REAL TAU,EFF,EPSS,KF,KOO,KPOO,KTOO
      COMMON ALPHA,BETA,TAU,INDEX1,INDEX2,FS,TF
      EFF=0.58
      IO=0.0258
```

```
      IF(INDEX2.EQ.4) GOTO 1190
      ED=15430.0 ; EP=2190.74 ; ET=352.793
      KD0=6.32E16 ; KP00=2.95E7 ; KT00=5.88E9
      GOTO 1200
1190  ED=29600/1.987 ; EP=6300/1.987 ; ET=2800/1.987
      KD0=5.95E13*60 ; KP00=7.0E6*50 ; KT00=3.52E9*60
1200  CONTINUE
      E=EP+0.5*(ED-ET)
      KF=KP00*EXP(-E/TF)*SQRT(2.0*EFF*I0*KD0/KT00)
C     TYPE*,KF
      DELTA=0.01
      DA=TAU*KF
      X3=(BETA*X1+ALPHA*DA*DELTA)/(1.+ALPHA*DA)
      T=TF*(1.0+X3)-273
      KT0=KT00*EXP(-ET/(TF*(1.+X3)))
      KP0=KP00*EXP(-EP/(TF*(1.+X3)))
      KD=KD0*EXP(-ED/(TF*(1.+X3)))
      ROM0=0.973-0.001154*(TF-273.0)
      EPSS=0.1945833+0.316565E-3*(TF*(1.+X3)-273.)
      ROM=0.973-0.001164*(TF*(1.+X3)-273.0)
      DR=ROM/ROM0
C     DR = 1.0
      BS = FS/(1.0 - FS)
      S = ((1.0 - EPSS * X1)/DR + BS)/(1.0 + BS)
C
      A=0.168-8.17E-06*(TF*(1.+X3)-887.0)**2
      B=0.03
      THETAT=3.372E-22/I0*EXP(1720.0/(TF*(1.0+X3)))
      THETAP=5.48E-16*EXP(14000.0/(TF*(1.0+X3)))

      LD0KP=S * X1/(1.0 - X1)/TAU
      PHIM=(1.-X1)/(1.-EPSS*X1 + BS)
      C=EXP(2.3*PHIM/(A+B*PHIM))
      KPKP0=1.-THETAP*LD0KP/C
      KP=KPKP0*KP0
      LD0=LD0KP/KP
      KTKT0=1./(1.+THETAT*KT0*LD0/C)
      KT=KTKT0*KT0
      TYPE 481,KTKT0,KPKP0
481   FORMAT(5X,'KTKT0=',E13.6,5X,'KPKP0=',E13.6)
C     -----------------------------------------------------------------
C     EVALUATION OF THE FUNCTION  F
C     -----------------------------------------------------------------
      IF(INDEX1.EQ.2)GOTO 115
      KT=KT0 ; KP=KP0
115   CONTINUE
      FUNC1=2.0*EFF*I0*(KP**2)*KD/KT*(TAU**2)
      IF(INDEX1.EQ.4) S = 1.0
      F2=( S * X1/(1.0 - X1))**2
      R =KD*TAU + S
      FUNC2=F2 * R
      FUN= (FUNC1)-(FUNC2)
C     TYPE*, X1, FUN
      RETURN
      END
```

```
      FVEC(2) = 2.0 * EFF * IO * TAU **2 * ( KP **2/KT * DKDDX1 - KP
     1          **2/KT **2 * KD * DKTDX1 + 2.0 * KP * KD/KT * DKPDX1)
     2          -( DF2DX1 * R + DRDX1 * F2 )

      FVEC31 = KP **2 * D2KD/KT - (KP/KT) **2 * DKDDX1 * DKTDX1 + 2.0*
     1         KP/KT * DKPDX1 * DKDDX1

      FVEC32 = KP **2 * KD/KT **2 * D2KT + (KP/KT) **2 * DKDDX1 * DKTD
     1         X1 + 2.0 * KP * KD/KT **2 * DKPDX1 * DKTDX1 - 2.0 * KP
     2         **2 * KD * DKTDX1 ** 2 /KT **3
      FVEC33 = KP * KD/KT * D2KP + KP/KT * DKDDX1 * DKPDX1 + KD/KT *
     1         DKPDX1 **2 - KP * KD/KT **2 * DKPDX1 * DKTDX1

      FVEC(3) = 2.0 * EFF * IO * TAU **2 * (FVEC31 - FVEC32 + 2.0 *
     1          FVEC33) - FVEC34
*----------------------------------------------------------------------
      TYPE 2 ,X1 , ALPHA1 , DA
      ALPHA1 = ALPHA * KF ; TAU1 = TAU/50.0
      TYPE 22, ALPHA1,TAU1
   22 FORMAT(' ALPHA1 = 'E13.6,3X,'TAU1 = 'E13.6/)
      TYPE 3 , FVEC(1) , FVEC(2) , FVEC(3)

    2 FORMAT( 2X,'X1= 'F10.7,3X,'ALPHA = 'E13.6,3X,'DA = 'F10.6/)
    3 FORMAT(5X,'FVEC(1) = 'E13.6 ,3X,'FVEC(2)= 'E13.6,3X'FVEC(3)=
     1   'E13.6/)
*----------------------------------------------------------------------
      RETURN
      END
```

```
DC2DX1 = 2.0 * (A + B * PHIM) * (DADX1 + B * DPHIM)
D2CDX1 = 2.3 * (C2 * DC1DX1 - C1 * DC2DX1)/C2 **2

DT11 = -THETAP * KP0/C **2 * D2CDX1 - DCDX1 * THETAP * DKP0DK/C
1       **2 - DCDX1 * KP0/C **2 * DTHEP + 2.0 * THETAP * KP0/C
2       **3 * DCDX1 **2
DT12 = THETAP/C * D2KP0 + DKP0DK/C * DTHEP - THETAP/C **2 *
1       DCDX1 * DKP0DX
DT13 = KP0/C * DTHEP2 + DKP0DK/C * DTHEP - KP0/C **2 * DTHEP *
1       DCDX1

DT1DX1 = DT11 + DT12 + DT13

DLDKP2 = ( X1 * D2S/(1.0 - X1) + 2.0 * DSDX1/(1.0 - X1)**2 + 2.0
1         * S/(1.0 - X1) **3 )/TAU

D2KP = D2KP0 - LDDKP * DT1DX1 - 2.0 * T1 * DLDKP - THETAP * KP0
1      /C * DLDKP2

DLD02 = DLDKP2/KP - 2.0 * DLDKP * DKPDX1/KP **2 - LDDKP * D2KP
1       /KP **2 + 2.0 * LDDKP/KP **3 * DKPDX1 **2

DP1 = THETAT * LD0 * KT0/C * (D2CDX1/C - (DCDX1/C )**2) + DCDX1*
1     DPDX1/C

DP2 = THETAT * LD0/C * D2KT0 - THETAT * LD0/C **2 * DKT0DX * DC
1     DX1 + THETAT/C * DLD0 * DKT0DX + LD0/C * DTHET * DKT0DX

DP3 = THETAT * KT0/C * DLD02 - THETAT * KT0/C **2 * DCDX1 * DLD0
1     + THETAT/C * DKT0DX * DLD0 + KT0/C * DTHET * DLD0

DP4 = LD0 * KT0/C * DTHET2 - LD0 * KT0/C **2 * DCDX1 * DTHET +
1     LD0/C * DKT0DX * DTHET + KT0/C * DLD0 * DTHET

D2PDX1 = -DP1 + DP2 + DP3 + DP4

D2KT = (P * D2KT0 - KT0 * D2PDX1)/P**2 - 2.0/P **3 * (P * DKT0DX
1      -KT0 * DPDX1) * DPDX1
      TYPE 19, DPDX1
      FORMAT(' DPDX1 = 'E13.6/)
```

```
C-------------------------------------------------------------------
C     CALCULATION OF THE FUNCTION VALUES
C-------------------------------------------------------------------
```

```
10    CONTINUE

F1 = KP **2 * KD/KT ; F2 = (S * X1/(1.0 - X1))**2
R = S + KD * TAU
DRDX1 = DSDX1 + TAU * DKDDX1
DF2DX1 = 2.0 * S * X1/(1.0 - X1)**2 * ( X1 * DSDX1 + S/(1.0-X1))

D2R = D2S + TAU * D2KD
D2F2 = 2.0 * S * X1/(1.0 - X1)**2 * (DSDX1 + X1 * D2S + 1/(1.0
1      -X1) **2 * (DSDX1 * (1.0 -X1) +S)) + 2.0 * ( DSDX1 * X1
2      + S/(1.0 - X1)) * ( DSDX1 * X1/(1.0 -X1) **2 + S * ( 1.
3      + X1)/(1.0 - X1) **3)

FVEC34 = D2F2 * R + 2.0 * DF2DX1 * DRDX1 + D2R * F2

FVEC(1) = 2.0 * EFF * T0 * TAU **2 * F1 - F2 * R
```

```
1          (1.0 + X3 ) ** 2 )

DTHET = -17200.0 * BETA * THETAP /( TF * (1.0 + ALPHA * DA) *
1          ( 1.0 + X3 ) ** 2 )

DADX1 = -16.34 E-6 * TF * BETA/( 1.0 + ALPHA * DA ) * (T - 337)

DF3DX1 = 0.001164 * TF * RJM * BETA/( 1.0 + ALPHA * DA)/RJM**2
DEPSX = EPSS + 0.916E-3 * BETA * TF * X1/( 1.0 + ALPHA * DA)
DSDX1 = ((1.0 - EPSS * X1 ) * DF3DX1 - F3 * DEPSX)/( 1.0 + BS)

DPHIM = ((1.0 - X1) * DEPSX -(1.0 + EPSS * X1 -)BS)/
1          (1.0 - EPSS * X1 + BS)**2

DCDX1 = 2.3 * C * ( A * DPHIM -| PHIM * DADX1)/(A + B * PHIM) **2

DLDKP = ( S/(1.0 - X1)**2 + DSDX1 * X1/(1.0 - X1))/TAU

DKPDX1 = DKPODX - LDDKP * (-DCDX1 * THETAP * KPO/C **2 +
1          (THETAP * DKPODX + KPO * DTHEP)/C) - THETAP * KPO/C *
2          DLDKP

DLDD  = (DSDX1 * X1/( KP * ( 1.0 - X1 )) - S * X1 * DKPDX1/
1          ( KP **2 * ( 1.0 - X1 )) + S /( KP * (1.0 - X1)**2))
2          /TAU

DPDX1  = -THETAP * LDD * KPO * DCDX1/C **2 + THETAP * LDD/C *
1          DKPODX + THETAP * KPO * DLDD/C + LDD * KPO/C * DTHET

DKTDX1 = ( P * DKPODX - KTO * DPDX1 )/P **2
```

---------------------------------------------------------------
CALCULATION OF THE SECOND DERIVATIVES
---------------------------------------------------------------

```
DENOM = TF * (1.0 + ALPHA * DA) * (1.0 + X3 ) **3
DTHEP2 = - 14000.0 * BETA /DENOM * (DTHEP * (1.0 + X3) - 2.0 *
1          THETAP * BETA/(1.0 + ALPHA * DA))

DTHET2 = -17200.0 * BETA /DENOM * (DTHET * (1.0 + X3 ) -2.0 *
1          THETAP * BETA/ ( 1.0 + ALPHA * DA))

T1   = -THETAP * KPO * DCDX1/ C **2 + (THETAP * DKPODX + KPO *
1          DTHEP)/C

D2ADX1 = -16.34 E-6 * (TF * BETA/ (1.0 + ALPHA * DA)) **2

D2F3 = 2.0 * DF3DX1 ** 2/F3

DEPSX2 = 1.832E-3 * TF * BETA/(1.0 + ALPHA * DA)

D2S = (D2F3 * (1.0 - EPSS * X1) - 2.0 * DF3DX1 * DEPSX - F3 *
1          DEPSX2) /(1.0 + BS)

R1 = (1.0 - X1) * DEPSX -1 + EPSS * X1 - BS
R2 = (1.0 - EPSS * X1 + BS) **2
DR1DX1 = (1.0 - X1) * DEPSX2
DR2DX1 = 2.0 * (1.0 - EPSS * X1 + BS) * ( - DEPSX)
DPHIM2 = ( R2 * DR1DX1 - R1 * DR2DX1)/R2 **2

C1 = C * (A * DPHIM - PHIM * DADX1) ; C2 = (A + B * PHIM)**2
DC1DX1 = C * (A * DPHIM2 - PHIM * D2ADX1) + DCDX1 * C1/C
```

```
      TYPE * ,KF
C------------------------------------------------------------------------
C     FIRST DERIVATIVS OF RATE CONSTANTS W. R. TO X1
C------------------------------------------------------------------------

      DTDX1 = TF * BETA /(1.0 + ALPHA * DA)
      DBT   = - DTDX1/T **2
      DKTODX = -KTO * ET * DBT
      DKPODX = - KPO * EP * DBT
      DKDDX1 = -KD * ED * DBT
C------------------------------------------------------------------------
C     SECOND DERIVATIVES OF THE RATE CONSTANTS
C------------------------------------------------------------------------
      DBT2 = 2.0 * (DTDX1) **2/ T **3
      D2KTO = -ET * (DKPODX * DBT + KTO * DBT2)
      D2KPO = -EP * (DKPODX * DBT + KPO * DBT2)
      D2KD  = -ED * (DKDDX1 * DBT + KD * DBT2)
C------------------------------------------------------------------------
C     SWITCH OVER TO NO GEL EFFECT CASE
C------------------------------------------------------------------------
      IF( NGEL . EQ . 2) GOTO 8
      KP = KPO ; KT = KTO ; DKPDX1 = DKPODX ; DKTDX1 = DKTODX
      D2KP = D2KPO ; D2KT = D2KTO ; D2KD = D2KD
      S = 1.0  ;  DSDX1 = 0.0 ; D2S = 0.0
      GOTO 10
C------------------------------------------------------------------------
C     CALCULATION OF THE PHYSICAL PROPERTIES FOR GEL EFFECT CASE
C------------------------------------------------------------------------
    8 CONTINUE

      ROMO = 0.973 - 0.001164 * ( TF - 273.0 )
      EPSS = 0.1945833 + 0.91666E-3 * ( T - 273.0 )
      ROM = 0.973 - 0.001164 * (T - 273.0 )
      F3 = ROMO/ROM
      DR = ROM/ROMO
C------------------------------------------------------------------------
      BS = FS/(1.0 - FS)              ! FS =  SOLVENT VOLUME FRACTION
      S = (BS + (1.0 - EPSS * X1 )/DR )/( 1.0 + BS)
      LDOKP =S * X1/(1.0-X1)/TAU      ! FROM MONOMER BALANCE
      TYPE * , LDOKP , S
      THETAP = 5.48 E-15 * EXP (14000.0/T)
      THETAT = 3.372 E-22/10 * EXP(17200.0/T)
      A =0.168 - 8.17E-06 * (T - 387.0)**2
      B = 0.03

      PHIM = ( 1.0 - X1 )/(1.0 - EPSS * X1 + BS )
      C    = EXP ( 2.3 * PHIM /( A + B * PHIM))
      KPO2 = THETAP*LDOKP/C*KPO
      KP = KPO - THETAP * KPO * LDOKP/C
      GP = KP/KPO
      LDO = LDOKP /KP
      TYPE*, THETAP,KPO,LDOKP,C
      P   = 1.0 + THETAP * LDO * KTO/C
      KT = KTO/P
      GT = KT/KTO
      TYPE 32, GP,GT
   32 FORMAT ( ' GP = 'E13.6,3X,' GT = 'E13.6/)
C------------------------------------------------------------------------
C     CALCULATION OF THE FIRST DERIVATIVE OF THE RATE CONSTANTS
C------------------------------------------------------------------------
      DTHEP = -14000.0 * BETA * THETAP /(TF * (1.0 + ALPHA * DA) *
```

```fortran
      WRITE(22,4) FS , BETA
      WRITE(22,1) FNORM,IFAIL,(X(J),J=1,3)
    1 FORMAT(2X,'FNORM=',E13.6/2X,'IFAIL=',I3/2X,'X(1)-,X(3)=',3E13.6)
    4 FORMAT(2X,'** FS =',F10.6,5X,'**   BETA =',F10.7//)
   55 FORMAT(5X,'TYPE IN THE VALUE OF NGEL'/5X,'NGEL=1 MEANS NO GEL
     1EFFECT'/5X,'NGEL = 2 MEANS GEL EFFECT'/)
      TYPE *,X(1),X(2),X(3),FNORM
   56 FORMAT(5X,'TYPE IN THE VALUE OF BETA'/)
   57 FORMAT(5X,'TYPE IN THE INITIAL GUESSES'/5X,'X(1),X(2),X(3)='/)
 1001 FORMAT(5X,'TYPE IN THE VALUE OF INDEX'/5X,'INDEX=1 MEANS CHOI
     1S RATE CONSTANTS'/5X,'INDEX=2 MEANS SOONGS RATE CONST.'/)
      IF(BETA.GT.1.0) STOP
      GOTO 801
      STOP
      END
```

```
C------------------------------------------------------------
C     SUBROUTINE FOR THE EVALUATION OF THE FUNCTIONS
C------------------------------------------------------------
```

```fortran
      SUBROUTINE  FCN (N, X, FVEC,IFLAG)
      REAL        X(N),  FVEC(N)
      INTEGER     NGEL,  INDEX, IFLAG,N
      REAL        IO,KF,KP,KPKPO,KT,KTKTO,KPOO,KTOO,KDO,KD,OOKP,LOO,
     1            TF,EFF,EPSS,ROM,ROMO,A,B,C,THETAP,THETAP
      COMMON      BETA,NGEL,INDEX,FS,TF
```

```
C------------------------------------------------------------
C     OPERATING CONDITIONS
      IO = 0.0258 ;   EFF = 0.58 ;  DELTA = 0.01
C------------------------------------------------------------
```

```fortran
      X1 = X(1) ; ALPHA = X(2) ; DA = X(3)
      X3 = (BETA * X1 + ALPHA * DA * DELTA)/(1.0 + ALPHA * DA)
      T  = TF * (1.0 + X3)
      IF  (INDEX .EQ. 1) GOTO 11
      IF  (INDEX .EQ. 2) GOTO  5
```

```
C------------------------------------------------------------
C*    CHOI'S RATE CONSTANTS
C*------------------------------------------------------------
```

```fortran
   11 KPOO = 4.2E08 ;  KTOO = 2.112E11 ; KDO = 3.57 E15
      EP   =3170.609 ; ET   = 1409.0595 ; ED =14896.829
      GOTO 6
```

```
C*------------------------------------------------------------
C*    SOONG'S RATE CONSTANTS
C*------------------------------------------------------------
```

```fortran
    5 KPOO = 2.95E07 ;  KTOO = 5.33E09 ;  KDO = 6.32E16
      EP   = 2189.23 ;  ET   = 352.793 ;  ED = 15430.3
```

```
C*------------------------------------------------------------
C*    RATE  EXPRESSIONS
C*------------------------------------------------------------
```

```fortran
    6 KP = KPOO * EXP(-EP/T)
      KT = KTOO * EXP(-ET/T)
      KD = KDO  * EXP(-ED/T)
```

```
C*------------------------------------------------------------
C*    DEFINITION OF DAMKOHLER NUMBER
C*------------------------------------------------------------
```

```fortran
      E = EP + 0.5 * (ED - ET)
      KF = KPOO * EXP(-E/TF) * SQRT( 2.0 * EFF * IO * KDO/KTOO )
      TAU = DA/KF
```

```
C     HYSTERESIS VARIETY FOR PMMA

C     DEFINITION OF VARIABLES
C     A , B      =   PARAMETER OF THE   FUJITA - DOOLITTLE CORRELATION
C                    FOR   (D/DO).
C     ALPHA      =   HEAT TRANSFER PARAMETER
C     BETA       =   HEAT GENERATION PARAMETER
C     DELTA      =   DIMENSIONLESS COOLANT TEMPERATURE
C     C          =   D/DO
C     D/DO       =   RATIO OF DIFFUSIVITIES  WITH GEL EFFECT TO THAT
C                    WITH  GEL EFFECT.
C     EFF        =   INITIATOR EFFICIENCY
C     EP         =   ACTIVATION ENERGY FOR PROPAGATION / R
C     ED         =   ACTIVATION ENERGY FOR INITIATOR DECOMP. / R
C     ET         =   ACTIVATION ENERGY FOR TERMINATION / R
C     FS         =   SOLVENT VOLUME FRACTION IN THE FEED
C     INDEX      =   PARAMETER INDICATING CHOI'S RATE CONSTANT FOR
C                    INDEX = 1 AND   SONG'S RATE CONSTANT FOR INDEX = 2
C     IO         =   INITIATOR CONCENTRATION , GM - MOL/LIT
C     NGEL       =   PARAMETER INDICATING GEL EFFECT FOR NGEL = 1 AND
C                    ABSENCE OF GEL EFFECT FOR NGEL = 2
C     KD         =   INITIATOR  DECOMPOSITION RATE CONSTANT
C     KDO        =   PRE - EXPONENTIAL PART OF  KD
C     KT         =   TERMINATION RATE CONSTANT
C     KTO        =   TERMINATION RATE CONSTANT IN ABSENCE OF GEL EFFECT
C     KTOO       =   PRE - EXPONENTIAL PART OF KTO
C     KP         =   PROPAGATION RATE CONSTANT
C     KPO        =   PROPAGATION RATE CONSTANT IN ABSENCE OF GLASS EFFECT
C     KPOO       =   PRE - EXPONENTIAL PART OF KPO
C     LOO        =   LIVE RADICAL POPULATION
C     LOOKP      =   PRODUCT OF  LOO  AND  KP
C     T          =   TEMPERATURE IN  DEG. K.
C     TF         =   FEED TEMPERATURE
C     DA         =   DAMKOHLER  NUMBER
C     PHIM       =   MONOMER VOLUME FRACTION
C     ROM        =   DENSITY OF THE MONOMER AT THE REACTOR TEMPERATURE
C     ROMO       =   DENSITY OF THE MONOMER AT THE FEED TEMPERATURE
C     EPSS       =   VOLUME CONTRACTION PARAMETER , ( ROP - ROMO/ROP
C     F3         =   ROMO / ROM
C     DR         =   DENSITY RATIO , ROM/ROMO
C     TAU        =   MEAN RESIDENCE TIME IN   MIN.
C     THETAP , THETAT  = PARAMETERS IN THE GLASS AND GEL EFFECT MODEL
C                    OF CHIU ET. AL. RESPECTIVELY
C     X1         =   MONOMER CONVERSION
C     X3         =   DIMENSIONLESS TEMPERATURE
C     DCDX1      =   FIRST DERIVATIVE OF C WITH RESPECT TO  X1
C     DADX1      =   FIRST DERIVATIVE OF A W.R. TO X1
C     D2ADX1     =   SECOND DERIVATIVE OF A W.R.  TO  X1
C     D2CDX1     =   SECOND DERIVATIVE OF C W.R.  TO X1
C     DTDX1      =   FIRST DERIVATIVE OF TEMPERATURE T W.R. TO  X1
C     DBT        =   FIRST  DERIVATIVE OF  (1/T)  W.R. TO  X1
C     DBT2       =   SECOND DERIVATIVE OF  (1/T)  W.R. TO  X1
C     D          =   FIRST DERIVATIVE OF LOO  W.R. TO X1
C     DLOKP      =   FIRST DERIVATIVE  OF  LOOKP  W.R. TO  X1
C     DLO02      =   SECOND DERIVATIVE OF  LOO  W.R. TO X1
C     DLOKP2     =   SECOND DERIVATIVE OF LOOKP  W.R. TO  X1
C     DKTDX1     =   FIRST DERIVATIVE OF KT W.R. TO  X1
C     DKTODX     =   FIRST DERIVATIVE OF KTO W.R. TO  X1
C     DKPDX1     =   FIRST DERIVATIVE OF KP W.R. TO  X1
C     DKPODX     =   FIRST DERIVATIVE OF KPO W.R. TO  X1
C     DKDDX1     =   FIRST DERIVATIVE OF KD  W.R. TO  X1
```

```
C      BATCH REATOR SIMULATION : RUNGE - KUTTA


       DIMENSION YPRIME(10) , Y(10)
       INTEGER RUNGE
       REAL    KP , KT ,KD , KPO , KTO , IO , LOOKP , LOO , L ,
      1        KPKPO , KTKTO
       OPEN    (UNIT = 22 , DEVICE = ' DSK ' , FILE = ' BATCH . OUT ')


       H = 0.001
       IREQ = 1000
       X    = 0.0
       XEND = 30.0
       ICOUNT = 1
       TF    = 300.0
       T     = 363.0
       IO    = 0.01548


C      INITIAL CONDITIONS

       Y(1) = 0.0
       Y(2) = IO
       Y(3) = 0.0


       WRITE(22, 100)
       WRITE(22, 200) T , IO
       WRITE(22, 300)
111    K = RUNGE (3 , Y , YPRIME , X , H)
       IF( K . NE. 1) GOTO 113
       X1 = Y(1)  ; I = Y(2) ; LOO = Y(3)

       KTO = 5.88 E9 * EXP( - 352.793/T )
       KPO = 2.95 E7 * EXP( -2190.74/T )
       KD  = 6.32 E16 * EXP( -15430.0/T )

       EPSS = 0.1945833 + 0.916567 E-3 * ( T - 273.0)
       EPSS = - EPSS
       A    = 0.168 - 8.17 E-06 * ( T - 387.0) ** 2
       B    = 0.03
       THETAP = 5.4814 E-16 * EXP( 13982.0/T )
       THETAT = 1.1353 E-22/IO * EXP( 17420.0 /T)

       PHIM = (1.0 - X1)/(1.0 + EPSS * X1)
       C = EXP( 2.303 * PHIM/(A + B * PHIM))

       KPKPO = 1.0/( 1.0 + THETAP * KPO * LOO/C)
       KTKTO = 1.0/( 1.0 + THETAT * KTO * LOO/C)

       KP = KPKPO * KPO
       KT = KTKTO * KTO

       EFF = 0.58
       YPRIME (1) = KP * (1.0 - X1 ) * LOO
       YPRIME (2) = -KD * I - KP * (1.0 - X1) * LOO * EPSS * 1/
      1             (1.0 + EPSS * X1)
```

```
      YPRIME (3) = 2.0 * EFF * KD * I -(KT * (LDO ** 2) - KP * (1.0
     1           - X1) * EPSS * (LDO **2)/(1.0 + EPSS * X1)
      GOTO 111
113   IF(X. GE. XEND) GOTO 116
      STOP
116   ICOUNT = ICOUNT + 1
      IF(ICOUNT . LT. IREQ) GOTO 111
      TYPE *    , X , X1 , I , LDO
      WRITE(22 , 400) X , X1
      ICOUNT = 1
      GOTO 111

100   FORMAT( 10X, 'BATCH REACTOR SIMULATION'//)
200   FORMAT( 10X,'TEMPERATURE = 'F10.6' DEG. K. '/10X,'INITIATOR
     1 LOADING = 'F10.5 ' MOL/L '//)
300   FORMAT(10X,'     TIME IN MIN.      ',5X,'MONOMER CONV.    '/)
400   FORMAT(20X,F10.6,10X,E13.6)

      END

C     SUBROUTINE RUNGE - KUTTA

      FUNCTION RUNGE ( N , Y , F , X , H)
      INTEGER   RUNGE
      DIMENSION PHI(50) , SAVEY(50) , Y(N) , F(N)
      DATA M/0/
      M = M + 1
      GOTO (1 , 2 , 3 , 4 , 5) , M
1     RUNGE = 1
      RETURN
2     DO 22 J = 1 , N
      SAVEY ( J ) = Y (J)
      PHI(J) = F(J)
22    Y(J) = SAVEY(J) + 0.5 * H * F(J)
      X = X + 0.5 * H
      RUNGE = 1
      RETURN

3     DO 33 J = 1, N
      PHI( J ) = PHI( J ) + 2.0 * F (J)
33    Y(J) = SAVEY(J) + 0.5 * H * F (J)
      RUNGE = 1
      RETURN
4     DO 44 J = 1, N
      PHI(J) = PHI(J) + 2.0 * F (J)
44    Y(J) = SAVEY( J) + H * F(J)
      X = X + 0.5 * H
      RUNGE = 1

5     DO 55 J = 1, N
55    Y(J) = SAVEY(J) + ( PHI(J) + F(J)) * H/6
      M = 0
```

```
RUNGE = 0
RETURN
END
```